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**REF-CITED:****U.S. PATENT DOCUMENTS**

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**ART-UNIT:** 152

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**ABSTRACT:**

Cosmetic skin and hair care compositions are provided containing amino-multicarboxylate starch derivatives as thickeners or emulsion stabilizers and which have the following formulas: ##STR1## wherein St-O represents a starch molecule;

R is H or CH.sub.3 ;

R' is H, CH.sub.3 or COOH;

M is a cation;

n is 2 or 3; and

R" is H or alkyl of 1 to 18 carbon atoms. These compositions have good rheological properties and have excellent aesthetic properties of feel and appearance.

16 Claims, 0 Drawing figures

Exemplary Claim Number: 1

**BRIEF SUMMARY:**

## (1) BACKGROUND OF THE INVENTION

(2) This invention relates to cosmetic compositions for the treatment of skin and hair comprising amino-multicarboxylate starch derivatives as a thickener and emulsion stabilizer.

(3) Various materials have been used to thicken and emulsion stabilize different cosmetic or personal care products. These materials include anionic derivatives of starch, xanthan gum and cellulose such as carboxymethylated starch or cellulose and phosphorylated starch and cellulose. Currently, Carbopol.RTM. resins, which are polyacrylic acid polymers produced by B. F. Goodrich, are the leading thickeners and emulsion stabilizers in the skin care and hair care markets.

(4) Besides possessing the necessary rheological properties, the cosmetic product with the added thickeners and emulsion stabilizers must also have suitable appearance and feeling on the skin. The starch derivatives of this invention are natural materials and in addition to the thickening and emulsion stabilizing properties, they provide cosmetic formulations with excellent aesthetic properties of skin feel and appearance.

## (5) SUMMARY OF THE INVENTION

(6) This invention is directed to cosmetic compositions which contain amino-multicarboxylate starch derivatives to provide thickening and emulsion stabilization and exhibit good appearance and feel to the skin.

(7) More particularly, this invention relates to cosmetic compositions which contain an effective emulsion stabilization or thickening amount of amino-multicarboxylate starch derivatives having the following structure: ##STR2## wherein St-O represents a starch molecule or a modified starch molecule (wherein the hydrogen of a hydroxyl group of an anhydroglucose unit has been replaced as shown);

(8) R is H or CH<sub>3</sub> ;

(9) R' is H, CH<sub>3</sub> OF COOH;

(10) M is a cation, more particularly H, alkali metal, alkaline earth metal or ammonium;

(11) n is 2 or 3; and

(12) R" is H or alkyl of 1 to 18 carbon atoms.

## (13) DETAILED DESCRIPTION OF THE INVENTION

(14) The starch derivatives (I) and (Ia) used in the cosmetic compositions of this invention are made by reacting starch with selected amino-multicarboxylic acid reagents having the following formula: ##STR3## where X is halogen;

(15) R is H or CH<sub>3</sub> ;

(16) R' is H, CH<sub>3</sub> or COOH;

(17) n is 2 or 3; and

(18) R" is H or alkyl of 1 to 18 carbon atoms.

(19) The reagents (II) and (IIa) as defined above are provided by a Michael reaction between an aminoalcohol and a selected ester containing an activated olefin followed by halogenation.

(20) The aminoalcohol used in preparing these reagents will generally have the formula ##STR4## where R is H or alkyl of 1 to 18, preferably 1 to 8 carbon atoms, n is 2 or 3, and the olefin containing ester will be any such ester, for example, alkyl acrylates, alkyl methacrylates or alkyl crotonates and more particularly will have the formula: ##STR5## where R is H or CH<sub>3</sub>, R' is H or CH<sub>3</sub> and R" is alkyl, and more particular, methyl, ethyl or propyl. Diesters of olefin containing esters, e.g., dialkyl maleates may be used to prepare the multicarboxylic acid reagents, particularly when the noted aminoalcohol has an alkyl R group.

(21) The formation of the multicarboxylate starch derivative (I) or (Ia) involves reacting the selected multicarboxylate reagent (II) or (IIa) with a starch base in an aqueous medium using either an aqueous slurry or an aqueous dispersion of the starch base. The reaction is carried out under alkaline conditions at a pH of from about 9.5 to 13, more particularly from about 10.5 to 12.5. The pH is conveniently controlled by the periodic addition of a dilute aqueous solution of sodium hydroxide or other common base including potassium hydroxide, calcium hydroxide, sodium carbonate, ammonium hydroxide, tetramethylammonium hydroxide, etc. The preferred bases are sodium and calcium hydroxide.

(22) The reaction is carried out at a temperature of from about 10.degree. to 95.degree. C., preferably from about 20.degree. to 50.degree. C. It will be recognized that the use of temperatures above about 60.degree. C. with granular starches in an aqueous medium will result in granule swelling and filtration difficulties or gelatinization of the starch.

(23) When conducting the reaction with granular starches, it may sometimes be desirable to carry out the reaction in the presence of salts, e.g., sodium sulfate, in amounts of from about 10 to 40% by weight, based on dry starch. The presence of sodium sulfate acts to suppress swelling of the starch and gives a more filterable product.

(24) The amount of multicarboxylate reagent (II) or (IIa) to be employed in the reaction will vary from about 0.1 to 100% by weight, based on the weight of dry starch, and depending on such factors as the starch base used, the particular multicarboxylate reagent used, the degree of substitution required in the end product, and to some extent, the reaction conditions used. In general, the preferred amount of reagent to be used when preparing the starch ether derivative containing amino-multicarboxylate groups is about 0.3 to 15% by weight for granular starches and about 15 to 75% by weight for non-granular starches.

(25) The multicarboxylate reagent may be added to the reaction mixture as a solid or an aqueous solution. The preferred concentration of the solution is 20 to 50% by weight, based on the weight of the reagent. In an alternative method, the carboxylate reagent solution is brought to the desired alkaline pH prior to its addition to the starch base. In this alternative method, the reagent is in the form of a salt rather than an acid or partially neutralized acid when it is introduced to the reaction mixture.

(26) Reaction time will vary from about 0.2 to 24 hours depending on such factors as the amount, stability and reactivity of the multicarboxylate reagent employed, the temperature, pH, the scale of reaction and the degree of substitution desired. In general, the preferred range of reaction time is from about 1 to 16 hours.

(27) After completion of the reaction, the pH of the reaction mixture is adjusted to from about 3 to 9 with any commercial acid such as hydrochloric acid, sulfuric acid, acetic acid, etc. Such acids may be conventionally added as a dilute aqueous solution. Depending on the final pH and the base used, the carboxyl group can be present as either the carboxylic acid, the corresponding salt or combination of the two (partially neutralized carboxyl groups). The cation M as found in starch derivatives (I) and (Ia) can be any cation and more particularly hydrogen, an alkali metal, an alkaline earth metal or ammonium. In the case of a multi-valent cation, e.g., calcium, the structure of the derivative could be cyclic.

(28) Recovery of the resulting starch ether derivatives may be readily accomplished, with the particular method employed being dependent on the form of the starch base. Thus, a granular starch is recovered by filtration or centrifugation, optionally washed with water to remove any residual salts, and dried. The granular starch products may also be drum-dried, spray-dried, or gelatinized and

isolated by alcohol precipitation or freeze drying to form non-granular products (i.e., gelatinized). If the starch product is non-granular, it may be purified by dialysis to remove residual salts and isolated by alcohol precipitation, freeze drying, or spray drying.

(29) The applicable starch bases which may be used in preparing the starch ether derivatives herein may be derived from any plant source including corn, potato, sweet potato, wheat, rice, sago, tapioca, waxy maize, sorghum, oat, high amylose corn, or the like. Also included are the conversion products derived from any of the latter bases including, for example, dextrans, prepared by the hydrolysis of acid and/or heat; oxidized starches prepared by treatment with oxidants such as sodium hypochlorite; fluidity or thin-boiling starches prepared by enzyme conversion or mild acid hydrolysis; and derivatized starches such as ethers and esters. Starch esters will undergo hydrolysis when exposed to reaction conditions needed to prepare starch ethers. If mixed starch ethers/esters are desired, it is obvious to those skilled in the art that the ether substituents must be reacted first, followed by esterification. The intermediate starch ether can be directly esterified or isolated and purified prior to esterification. The starch base may be a granular starch or a gelatinized starch, i.e., non-granular starch.

(30) The preferred starch derivatives (I) and (Ia) of this invention as described above, are those wherein R, R', and R" are hydrogen, M is hydrogen and n is 2 and more particularly those having the structure (I). The starch base is preferably potato starch. Also the starch base and the resulting starch derivatives may be further derivatized or modified with other groups such as cationic groups. Particularly useful cationic starches are the tertiary aminoalkyl starch ethers such as 2-diethylaminoethyl chloride and quaternary ammonium starch ethers such as 2,3-epoxypropyltrimethylammonium chloride.

(31) The amino-multicarboxylate starch derivatives and the method of preparation are further described in copending application Ser. No. 08/190,824 filed Feb. 2, 1994, which is incorporated herein by reference.

(32) The amino-multicarboxylate starch derivatives (I) and (Ia) are especially useful in cosmetic compositions such as skin care or hair care compositions where they provide thickening and emulsion stabilizing properties and other rheological and aesthetic properties. The skin and hair care compositions of this invention may involve different media or systems and will comprise a suitable cosmetic vehicle or base for the composition. This vehicle may be an emulsion, an aqueous system, a solvent system or a combination of aqueous and solvent systems.

(33) The emulsions are the preferred vehicle or base for the

cosmetic compositions of this invention and products of this type include the skin care creams and lotions. These emulsions which comprise water-based and oil-based phases, may be oil-in-water emulsions having oil as the dispersed phase and water as the continuous phase or they may be water-in-oil emulsions with water dispersed in oil, which is the continuous phase. The oil phase, which may comprise from about 10 to 90% by weight of the composition, is typically made up of cosmetically acceptable or conventional oily substances that are soluble in this phase, such as oils, waxes and emulsifiers. Compounds which can be included in the oil phase are typically mineral, animal and vegetable oils and fats, synthetic esters, fatty acids, aliphatic alcohols, higher fatty alcohols, alkyl amines, waxes, so called mineral fats and oils, such as paraffin oil, petrolatum, ceresin, silicone oils and silicone fats. The water phase may comprise from about 10 to 90% by weight of the composition and this will include water and water soluble components such as alkalis, alkanolamines, polyhydric alcohols and preservatives. These emulsions include one or more emulsifiers which usually are contained in the oil phase but in some instances, depending on the type, may be in the water phase. The starch derivatives (I) and (Ia) may be used to stabilize the emulsion or to replace secondary emulsifiers. Other emulsifiers which can be used may be ionic or nonionic are well known and constitute a large group of conventional and commercially available products. They are often characterized by their hydrophilic-lipophilic balance (HLB). Oil-in-water (O/W) emulsifying agents typically have an HLB of more than 6.0 and produce emulsions in which the continuous phase is hydrophilic and such emulsions are generally dispersible in water. Emulsifiers of this type include PEG 300 distearate, sorbitan monolaurate and triethanolamine stearate. Water-in-oil (W/O) emulsifiers usually have an HLB of less than 6.0, preferably below 5, and produce emulsions in which the continuous phase is lipophilic. Such emulsifiers include, lanolin alcohols, ethylene glycol monostearate, sorbitan mono-oleate and PEG 200 dilaurate. Emulsifiers with HLB's of between 5 and 7 may function as either W/O or O/W emulsifiers depending on how they are used.

(34) The amount of emulsifier used in the emulsions of this invention including the starch derivatives (I) and (Ia) can vary depending on the system and typically will be an effective emulsifying amount. More particularly, the amount of emulsifier can vary from about 0.1 to 25% by weight of the composition and preferably from about 1 to 10%.

(35) Various other ingredients and additives may be included in one or both of the oil and water phases in the cosmetic skin care emulsions described above. This includes emollients, humectants, thickening agents, UV-light inhibitors, preservatives, pigments, dyes, colorants, alpha hydroxy acids, aesthetic enhancers such as starch, perfumes and fragrances, film formers (water proofing agents) antiseptics, antifungal, antimicrobial and other medicaments and

solvents. Effective amounts of one or more of these and other active and functional ingredients is generally used and this can total from about 0.1 to 25% by weight of the composition and more particularly from about 0.1 to 15%.

(36) Other cosmetic compositions using the selected starch derivatives in accordance with this invention involve aqueous or solvent systems wherein the added components are soluble or dispersible therein. The aqueous system will comprise the selected starch derivatives, additives and active and functional ingredients, optionally a propellant and the balance water. Generally, an aqueous system will comprise from about 10 to 99.8% by weight water, preferably 50 to 80%, from about 0.1 to 20% by weight of the starch derivative, preferably 0.3 to 5%, from about 0.1 to 25% by weight of additives and ingredients, preferably 0.1 to 15% and from about 0 to 50% by weight of propellant, preferably 0 to 30%. Compositions of this type include the topical sprays and products containing fragrances and antimicrobial agents.

(37) The topical sprays include the aerosol sprays or products containing a propellant. While any of the known propellants may be used in the compositions of this invention, preferred propellants included the non-halogenated hydrocarbons, particularly the lower boiling hydrocarbons such as C.sub.3 -C.sub.6 straight and branched chain hydrocarbons, i.e., propane, butane, isobutane and mixtures thereof. Other preferred propellants include the ethers, such as dimethyl ether, hydrofluorocarbon and the compressed gases such as N.sub.2 and CO.sub.2.

(38) The use of a solvent system as the vehicle or base involves other cosmetic compositions containing the selected starch derivative to provide thickening and/or emulsion stabilizing properties. The solvent system will comprise the selected starch derivative, additives and active and functional ingredients, optionally a propellant and the balance solvent. The solvent may be any of the known organic solvents which may solubilize or disperse components of the skin care composition and more particularly aliphatic alcohols, esters, ethers, ketones, amines and hydrocarbons including the aromatic, nitrated and chlorinated hydrocarbons. Particularly preferred organic solvents are the lower aliphatic alcohols such as the C.sub.1-3 alcohols and especially ethanol. Generally the solvent system will comprise from about 25 to 99.8% by weight of solvent, preferably 50 to 80%, from about 0.1 to 20% by weight of the starch derivatives, preferably 0.3 to 5%, from about 0.1 to 25% by weight of additives and ingredients, preferably 0.1 to 15% and from about 0 to 75% by weight of propellant, preferably 0 to 35%.

(39) The additives and other ingredients which may be included in either the aqueous or solvent based systems are the same as those described above for the emulsion and oil based systems. The



propellants which may be included in the solvent system are the same as those described above for the aqueous systems. Additionally, a mixture of the aqueous and solvent systems may be used wherein water and solvent, especially alcohols are combined along with the components, i.e., starch derivative, additives and propellant. Such a composition will comprise 25 to 99.8% by weight of a combination of water and solvent, preferably 50 to 80% along with the components as described above.

(40) The amino-multicarboxylate starch derivatives (I) and (Ia) used in cosmetic compositions in accordance with this invention will comprise an effective thickening or emulsion stabilizing amount. More particularly the amino-multicarboxylate starch derivative will comprise from about 0.1 to 20% and preferably from about 0.3 to 5% by weight of the cosmetic composition.

(41) Preparation of the cosmetic emulsion compositions typically involves adding the oil soluble components in one vessel and heating to, e.g., 75.degree. to 80.degree. C. and combining the water soluble components in another vessel and heating to, e.g., 75.degree. to 80.degree. C. Depending on whether O/W or W/O emulsions are being prepared the warmed inner phase is then slowly added to the outer phase with agitation.

(42) The following examples further illustrate the embodiments of this invention. In the examples all parts and percentages are given by weight and all temperatures in degrees Celsius unless otherwise noted.

#### **DETAILED DESCRIPTION:**

##### (1) EXAMPLE I

(2) This example illustrates the preparation of starch modified with an amino-multicarboxylic acid reagent, i.e., 2-chloroethylaminodipropionic acid (hereinafter referred to as CEPA).

(3) Overhead stirring was used throughout this reaction. Deionized water (150 mL) was added to a one liter beaker and heated to 45.degree. C. with an external constant temperature bath. Sodium sulfate (30 g; 30% on starch) was dissolved in the water followed by the addition of potato starch (100 g) into the solution in portions to form a uniform slurry. A solution of 3% aqueous sodium hydroxide (25 mL) was added slowly with good agitation to minimize starch swelling. A 25% aqueous solution of CEPA reagent (32 mL) to give an 8% starch treatment (dry basis) was added simultaneously with a 3% aqueous sodium hydroxide solution (170 mL) at addition rates that kept the level of caustic high (pH of about 11.0 to 11.5) in the reaction. The reaction was run at 42.degree. to 45.degree. C. for 16

hours and then neutralized with addition of 3 N HCl to a pH of about 6.5 followed by stirring for 30 minutes. The starch was then filtered and washed two times with 150 mL of water and allowed to air dry. Analysis of the starch for bound nitrogen showed 0.25% N (dry basis) indicating that the starch had been modified with the aminodicarboxylic acid reagent (CEPA).

(4) A 1% starch cook of the CEPA starch derivative prepared above was made (1 g of the derivative in 99 mL of deionized H.sub.2 O) for 20 minutes. The cook of the CEPA potato starch thickened within a minute and produced a translucent gel with a smooth consistency and an excellent non-tacky conditioning skin feel. The starch was also salt-sensitive causing it to "break" on the skin surface and rub in very well.

(5) EXAMPLE II

(6) The CEPA potato starch derivative described in Example I was formulated into a cosmetic lotion in the following manner:

(7) An oil phase (Phase A) and water phase (Phase B) having the following ingredients were prepared and along with the preservative of Phase C, Germaben II E a product of Sutton Laboratories, which is a combination of propylene glycol (and) diazolidinyl urea (and) methylparaben and propylparaben, were combined and mixed to form a cosmetic lotion:

|                           |                                |                               |
|---------------------------|--------------------------------|-------------------------------|
| (1)                       |                                | PARTS BY WEIGHT               |
|                           |                                | PHASE A Cetyl alcohol 1.0     |
| Octyl palmitate 5.0       | C.sub.12-15 alkyl benzoate 5.0 | Stearic acid T.P. 2.0         |
| Dimethicone copolyol 1.0  | PHASE B Deionized water 79.5   |                               |
| Triethanolamine (99%) 0.5 | Propylene glycol 3.0           | CEPA potato <u>starch</u> 2.0 |
| PHASE C Germaben II E 1.0 |                                |                               |

(8) The above sample containing the CEPA modified potato starch and identified as Sample A was compared to control samples, Control-1 without the CEPA starch derivative and containing no thickener (Carbopol) or secondary emulsifier and Control-2 without the CEPA starch derivative but containing Carbopol and secondary emulsifiers. Also evaluated were two samples containing the CEPA potato starch, one without Carbopol (Sample B) and one without secondary emulsifiers (Sample C). The formulations are shown below:

|                                    |                     |                                   |
|------------------------------------|---------------------|-----------------------------------|
| (2)                                |                     | SAMPLES CONTROL CONTROL A B C 1 2 |
| PHASE A Cetyl Alcohol 1.0          | 1.0 1.0 1.0 1.0 1.0 | Ceteth 20 -- 1.0 -- -- 1.0        |
| Glyceryl stearate SE --            | 1.0 -- -- 1.0       | Octyl palmitate 5.0 5.0 5.0 5.0   |
| 5.0 C.sub.12-15 alkyl benzoate 5.0 | 5.0 5.0 5.0 5.0     | Stearic acid T.P.                 |

2.0 2.0 2.0 2.0 2.0 Dimethicone copolyol 1.0 1.0 1.0 1.0 1.0 PHASE B  
 Deionized water 79.5 77.5 78.5 81.5 78.5 Carbopol 940 -- -- 0.5 --  
 0.5 Triethanolamine (99%) 0.5 0.5 1.0 0.5 1.0 Propylene glycol 3.0  
 3.0 3.0 3.0 3.0 CEPA potato starch 2.0 2.0 2.0 -- -- PHASE C Germaben  
 II E 1.0 1.0 1.0 1.0 1.0

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(9) All of the above samples were placed in standard laboratory stability studies (one month)-ambient, oven (45.degree. C.), freeze/thaw and refrigerator. Control 1 failed after 24 hours at 45.degree. C., the emulsion splitting into phases. All other formulations passed the stability study. Aesthetically, sample formulation A, CEPA potato starch replacing Carbopol and without secondary emulsifiers had the best skin feel and appearance. This formulation had a very soft, conditioning, non-tacky feel and a nice white glossy look. Sample A and Control-2 were placed in accelerated viscosity studies at 45.degree. C. and ambient temperature. Results are shown below:

| (3)         | VISCOSITY cP TIME SAMPLE |               |          |        |        |         |          |  |  |  |
|-------------|--------------------------|---------------|----------|--------|--------|---------|----------|--|--|--|
| A CONTROL 2 | Ambient Initial          |               |          |        |        |         |          |  |  |  |
| 16,670      | 34,750                   | 45.degree. C. | Initial  | 17,000 | 33,166 | Ambient | 1 week   |  |  |  |
| 22,000      | 34,000                   | 45.degree. C. | 1 week   | 17,500 | 17,583 | Ambient | 2 weeks  |  |  |  |
| 22,500      | 34,644                   | 45.degree. C. | 2 weeks  | 20,000 | 23,416 | Ambient | 8 weeks  |  |  |  |
| 21,500      | 33,083                   | 45.degree. C. | 8 weeks  | 13,000 | 27,500 | Ambient | 11 weeks |  |  |  |
| 22,000      | 32,166                   | 45.degree. C. | 11 weeks | 15,666 | 15,588 | Ambient | 20 weeks |  |  |  |
| 19,000      | 27,416                   | 45.degree. C. | 20 weeks | 11,083 | (65%)  | 7,083   | (21%)    |  |  |  |

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(10) The viscosity studies indicate that the CEPA potato starch Sample (A) is relatively stable over time and is actually superior to the Carbopol standard (Control 2). The CEPA potato starch sample maintained 65% of its viscosity at 45.degree. C. while the Carbopol sample maintained only 21%.

(11) EXAMPLE III

(12) A moisturizing hand and body lotion containing the CEPA potato starch derivative described in Example I was formulated and had the following ingredients:

| (4)                           | Parts by Weight |                                      |               |                         |                |         |  |  |  |  |
|-------------------------------|-----------------|--------------------------------------|---------------|-------------------------|----------------|---------|--|--|--|--|
| Phase A N-butyl stearate 8.00 |                 |                                      |               |                         |                |         |  |  |  |  |
| C.sub.12-15 alkyl benzoate    | 2.00            | Cetearyl octanoate                   | 5.00          | Isopropyl               |                |         |  |  |  |  |
| palmitate                     | 5.00            | Stearic acid T.P.                    | 2.00          | Cetyl alcohol           | 1.00           | Lanolin |  |  |  |  |
| alcohol                       | 0.50            | Dimethicone copolyol                 | 1.00          | Cyclomethicone          | 3.00           | Phenyl  |  |  |  |  |
| trimethicone                  | 1.00            | Tocopherol acetate                   | 1.00          | Phase B Deionized water |                |         |  |  |  |  |
| 59.25                         | Methylparaben   | 0.15                                 | Propylparaben | 0.10                    | Trisodium EDTA | 0.05    |  |  |  |  |
| Triethanolamine (99%)         | 0.80            | Acrylates/octyl acrylamide copolymer | 1.00          |                         |                |         |  |  |  |  |
| CEPA potato <u>starch</u>     | 4.00            | Phase C Propylene glycol             | 3.00          | Aluminum <u>starch</u>  |                |         |  |  |  |  |

octenyl-succinate 2.00 Phase D Diazolidinyl urea 0.15 100.00

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(13) The ingredients of Phase B except for the acrylate/acrylamide copolymer and aluminum starch octenyl-succinate were heated to 80.degree. C. and the acrylate/acrylamide copolymer was slowly added with mixing until the addition was complete. The ingredients of Phase A were combined and heated to 80.degree. C. and then added to Phase B while maintaining the temperature at 80.degree. C. and mixing for 15 minutes. The mixture was then cooled to 40.degree. C. Aluminum starch octenyl-succinate was slurried into propylene glycol and then added to the combined mixture at 40.degree. C. and then Phase D was added and mixed until uniform. The formulation was then cooled to room temperature. This example shows the use of the CEPA potato starch derivative as a thickener and emulsion stabilizer.

(14) EXAMPLE IV

(15) A sunscreen composition containing an inorganic zinc oxide sun block and the CEPA potato starch derivative of Example I was formulated and had the following ingredients:

| (5)                      | Parts by Weight                |
|--------------------------|--------------------------------|
|                          | Phase A Octyl methoxycinnamate |
| 7.50 DEA cetyl phosphate | 1.50 Cyclomethicone            |
| 2.00 Cetearyl alcohol    | 1.00 Tocopherol acetate        |
| 0.50 Cetearyl octanoate  | 8.00 Phase B                   |
| Deionized water          | 67.40 Trisodium EDTA           |
| 0.10 Propylene glycol    | 3.00 CEPA potato <u>starch</u> |
| 2.00 Phase C Zinc oxide  | 6.00 Phase D Germaben II E     |
| 1.00                     | 100.00                         |

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(16) The ingredients of Phase B were combined with CEPA potato starch added slowly and then heated to 80.degree. C. and mixed thoroughly. Phase A was combined and heated to 80.degree. C. with mixing and then added to Phase B and mixed for 15 minutes. Then Phase C was added, mixed thoroughly and cooled to 40.degree. C. followed by addition of Phase D with mixing. The CEPA starch derivative effectively viscosified a zinc oxide based system.

(17) EXAMPLE V

(18) A sunscreen composition (SPF 6) using an organic UV absorbing sunscreen was formulated and had the following ingredients:

| (6)                            | Parts by Weight                |
|--------------------------------|--------------------------------|
|                                | Phase A Octyl methoxycinnamate |
| 7.50 Octyl palmitate           | 5.00 Cetyl alcohol             |
| 1.00 Stearic acid T.P.         | 2.00 Dimethicone copolyol      |
| 1.00 Phase B Deionized water   | 80.60 Methylparaben            |
| 0.15 Propylparaben             | 0.10 Triethanolamine (99%)     |
| 0.50 CEPA potato <u>starch</u> | 2.00 Phase C Diazolidenyl urea |
| 0.15                           | 100.00                         |

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(19) The CEPA potato starch was added to Phase B ingredients and heated to 80.degree. C. Phase A was combined, heated to 80.degree. C. and then added to Phase B with mixing for 15 minutes. The mixture was cooled to 40.degree. C., Phase C added and mixed thoroughly and the formulation then cooled to room temperature. This example illustrates a thickened, low surfactant containing sunscreen.

(20) EXAMPLE VI

(21) A shave cream composition containing the CEPA potato starch derivative of Example I was formulated with the following ingredients:

(7) \_\_\_\_\_ Parts by Weight  
Phase A Stearic Acid T.P. 8.00  
Phase B Deionized water 76.80 Sodium lauryl sulfate 7.00  
Triethanolamine (99%) 5.00 CEPA potato starch 2.00 Phase C Germaben  
II E 1.00 [Propylene glycol (and) diazolidinyl urea (and)  
methylparaben (and) propylparaben] Phase D Fragrance 0.20 100.00

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(22) The ingredients of Phase B were combined and heated to 80.degree. C. In a separate vessel Phase A was heated to 80.degree. C., then added to Phase B and mixed for 15 minutes. The mixture was cooled to 40.degree. C., Phases C and D added with thorough mixing. After cooling to room temperature, the formulation was packaged in aerosol cans (96.5% concentrate of above formulation and 3.5% propellant A-46). This example illustrates the use of CEPA potato starch to effectively thicken a propellant based shave cream.

(23) EXAMPLE VII

(24) Another cosmetic composition, an after shave balm which contained the CEPA potato starch of Example I was formulated with the following ingredients:

(8) \_\_\_\_\_ Parts by Weight  
Phase A N-butyl stearate 4.00  
Cetyl palmitate 2.50 Myristyl propionate 3.00 Mineral Oil/PEG-30 1.50  
Lanolin/Cetyl Alcohol Phase B Deionized water 69.60 Lecithin 1.00  
CEPA potato starch 2.00 NaOH (25%) 0.40 Methylparaben 0.15  
Propylparaben 0.15 Phase C Glycerin 7.00 Aluminum starch octenyl  
succinate 8.00 Phenoxyethanol 0.20 Phase D Fragrance 0.50 100.00

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(25) The CEPA potato starch was dispersed in Phase B ingredients and heated to 80.degree. C. Phase A ingredients were combined, heated

to 80.degree. C. and added to Phase B with mixing (15 minutes). After cooling to 40.degree. C., aluminum starch octenyl succinate and glycerin were added followed by the addition of phenoxyethanol with thorough mixing. Phase D was added and the formulation mixed until uniform. This formulation represents an effectively thickened after shave balm emulsion.

(26) EXAMPLE VIII

(27) A cosmetic lotion for skin treatment containing alpha hydroxy acid and the CEPA potato starch of Example I was formulated with the following ingredients:

| (9)                            | Parts by Weight                  |
|--------------------------------|----------------------------------|
|                                | Phase A Isopropyl palmitate      |
| 6.50 Stearic acid T.P.         | 4.00 Glyceryl stearate           |
| 2.00 Cetyl alcohol             | 1.50 Isostearic acid             |
| 1.00 Dimethicone               | 1.00 PEG 40                      |
| stearate                       | 0.50 Phase B Deionized water     |
| 68.55 Ammonium hydroxide (28%) |                                  |
| 2.00 CEPA potato <u>starch</u> | 2.00 BHA                         |
| 0.10 Sorbitan stearate         | 0.50 Phase C                     |
| Glycolic acid (70% solution)   | 8.00 Phase D Imidazolidinyl urea |
| 0.35                           |                                  |
| 100.00                         |                                  |

(28) Phase B ingredients were combined and heated to 80.degree. C. Phase A ingredients were combined, heated to 80.degree. C., added to Phase B and mixed for 15 minutes. After cooling to 50.degree. C., Phase C was added with mixing and then Phase D added with thorough mixing. The formulation was cooled to room temperature and illustrates the use of CEPA potato starch to thicken a low pH, alpha hydroxy acid emulsion.

(29) EXAMPLE IX

(30) A liquid talc, solvent based cosmetic composition containing the CEPA potato starch of 15 Example I was formulated with the following ingredients:

| (10)                    | Parts by Weight                 |
|-------------------------|---------------------------------|
|                         | Phase A Cetearyl alcohol        |
| 0.50                    |                                 |
| PPG 3 myristyl ether    | 0.25 Emulsifying wax N.F.       |
| 2.50 Phase B Deionized  |                                 |
| water                   | 64.50 CEPA potato <u>starch</u> |
| 2.00 Anhydrous ethanol  | 20.00                           |
| Polysorbate 80 (and)    | 0.25 cetyl acetate (and)        |
| acetylate lanolin       |                                 |
| alcohol Phase C Tapioca | 10.0 100.0                      |

(31) Deionized water and CEPA potato starch were combined, heated to 80.degree. C., mixed for 10 minutes and after cooling to 60.degree. C. the remaining Phase B ingredients were added. Phase A ingredients were combined, heated to 60.degree. C. and added to Phase B with mixing. The mixture was cooled to 50.degree. C., Phase C added

with mixing and then cooled to room temperature. This formulation represents an effectively thickened solvent (ethanol) based system.

**CLAIMS:**

What is claimed is:

1. A cosmetic skin care or hair care composition comprising a cosmetic vehicle and from about 0.1 to about 20% by weight of an amino multicarboxylate starch derivative having the following structure: ##STR6## wherein St-O represents a starch molecule;

R is H or CH<sub>3</sub> ;

R' is H, CH<sub>3</sub> or COOH;

M is a cation selected from the group consisting of hydrogen, alkali metal, alkaline earth metal and ammonium;

n is 2 or 3; and

R" is H or alkyl of 1 to 18 carbon atoms.

2. The composition of claim 1 wherein each R, R' and R" are H and M is H.

3. The composition of claim 2 wherein n is 2.

4. The composition of claim 3 wherein the starch derivative has the structure (I).

5. The composition of claim 4 wherein the starch is potato starch.

6. The composition of claim 4 wherein from about 0.3 to 5% by weight of the starch derivative is used based on the weight of the cosmetic composition.

7. The composition of claim 6 wherein the starch is potato starch.

8. The cosmetic composition of claim 1 wherein the cosmetic vehicle is an emulsion, an aqueous system, a solvent system or a mixture of aqueous and solvent systems.

9. The composition of claim 8 wherein the cosmetic vehicle comprises an emulsion of about 10 to 90% by weight of an oil phase and about 10 to 90% by weight of a water phase.

10. The composition of claim 9 wherein each R, R' and R" are H and M is H.

11. The composition of claim 10 wherein n is 2.

12. The composition of claim 11 wherein the starch derivative has the structure (I).

13. The composition of claim 12 wherein from about 0.1 to 20% by weight of the starch derivative is used based on the weight of the cosmetic composition.

14. The composition of claim 13 wherein the starch is potato starch.

15. The composition of claim 12 wherein 0.3 to 5% by weight of the starch derivative is used based on the weight of the cosmetic composition.

16. The composition of claim 15 wherein the starch is potato starch.



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**DOCUMENT-IDENTIFIER:** US 6365002 B1  
**TITLE:** Amphoteric starches used in papermaking  
**DATE-ISSUED:** April 2, 2002

**INVENTOR-INFORMATION:**

| NAME              | CITY       | STATE | ZIP | CODE | COUNTRY |
|-------------------|------------|-------|-----|------|---------|
| Bindzus; Wolfgang | Belle Mead | NJ    | N/A |      | N/A     |
| Altieri; Paul A.  | Belle Mead | NJ    | N/A |      | N/A     |

**ASSIGNEE INFORMATION:**

| NAME                                                                  | CITY          | STATE | ZIP  | COUNTRY | TYPE |
|-----------------------------------------------------------------------|---------------|-------|------|---------|------|
|                                                                       |               |       | CODE |         | CODE |
| National <u>Starch</u> and Chemical<br>Investment Holding Corporation | New<br>Castle | DE    | N/A  | N/A     | 02   |

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**REF-CITED:****U.S. PATENT DOCUMENTS**

| PAT-NO         | ISSUE-DATE   | PATENTEE-NAME   | US-CL           |
|----------------|--------------|-----------------|-----------------|
| <u>4166173</u> | August 1979  | Wurzburg et al. | 536/109 N/A N/A |
| <u>4216310</u> | August 1980  | Wurzburg et al. | 536/109 N/A N/A |
| <u>4876336</u> | October 1989 | Solarek et al.  | 536/109 N/A N/A |

**OTHER** U.S. application No. 09/633,832, Bindzus et al.,  
**PUBLICATIONS** filed Aug. 7, 2000.

**ART-UNIT:** 1731

**PRIMARY-EXAMINER:** Chin; Peter

**ATTY-AGENT-FIRM:** Duncan, Esq.; Laurelee Zagarella, Jr.; Eugene

**ABSTRACT:**

The use in papermaking of an amphoteric starch additive which contains a phosphate functional group and is made under anhydrous conditions while in a fluidized state, provides advantageous paper properties and improved wet end performance.

21 Claims, 0 Drawing figures

Exemplary Claim Number: 1

**BRIEF SUMMARY:**

(1) BACKGROUND OF THE INVENTION

(2) This invention relates to a process of papermaking wherein amphoteric starch containing a phosphate component and made by a select process is added to the wet end of the papermaking system to provide paper with good drainage and other improved properties.

(3) The term "paper" as used herein, includes sheet-like masses and molded products made from fibrous cellulosic material, which may be derived from natural sources, synthetics such as polyamides, polyesters, rayon and polyacrylic resins as well as from mineral fibers such as asbestos and glass. In addition, paper made from combinations of cellulosic and synthetic materials are applicable herein. Paperboard is also included within the broad term "paper".

(4) Papermaking, as it is conventionally known, is a process of introducing an aqueous slurry of pulp or wood cellulosic fibers (which have been beaten or refined to achieve a level of fiber hydration and to which a variety of functional additives can be added) onto a screen or similar device in such a manner that the water is removed, thereby forming a sheet of the consolidated fibers, which upon pressing and drying can be processed into dry roll or sheet form. Two well known papermaking processes involve the Fourdrinier machine, the most common, and the cylinder machine. In the Fourdrinier and multicylinder operations, and in other machine operations, as typical in papermaking, the feed or inlet to the machine is an aqueous slurry or water suspension of pulp fibers which is provided from what is called the "wet end" system. In the wet end, the pulp along with other additives are mixed in an aqueous slurry and subject to mechanical and other operations such as beating and refining to improve interfiber bonding and other physical properties of the finished sheet. Additives commonly introduced along with the pulp fibers are pigments such as titanium dioxide, mineral fillers such as clay and calcium carbonate and other materials introduced into paper to achieve such properties as improved brightness, opacity, smoothness, ink receptivity, fire retardance, water

resistance, increased bulk, etc.

(5) It has been known to add various materials, including starch, to the pulp, or stock in the papermaking process or prior to the formation of the sheet, to aid in retention, drainage and strength properties.

(6) Starch has been used in the paper industry for many years and, in fact, is the second largest volume raw material component in paper. Starches perform a number of functions in papermaking including strength improvement, increased drainage and increased retention of fibers, fines and other components on the wire. Both unmodified and modified types of starch have been used.

(7) Anionic and cationic starches as well as amphoteric starches have long been used as additives in papermaking for their contributions to strength and pigment retention in the paper. See, for example, U.S. Pat. No. 3,459,632 issued to C. Caldwell et al. on Aug. 5, 1969 and U.S. Pat. No. 3,562,102 issued to K. Moser et al. on Feb. 9, 1971. More recent patents involving the use of starches in papermaking include U.S. Pat. No. 4,876,336 issued to D. Solarek et al. on Oct. 24, 1989 and which discloses the use of amphoteric starch derivatives and U.S. Pat. No. 5,129,989 issued to S. Gosset et al. on Jul. 14, 1992 which discloses the use of cationic and anionic starches in separate additions.

(8) While starch additives of the prior art have shown favorable effects in improving paper properties, it has been found that the use of amphoteric starch additives, prepared as described herein, have high levels of phosphorus substitution, maintain high viscosities, minimize residual salts and other impurities and improve the wet end performance in papermaking operations.

(9) SUMMARY OF THE INVENTION

(10) Now it has been found that the use in papermaking of an amphoteric starch additive which contains a phosphate component and which is made under anhydrous conditions while in a fluidized state, provides advantageous paper properties and improved wet end performance.

(11) More particularly, this invention involves the process of making paper comprising adding to the paper stock prior to or during formation of the sheet, an effective amount of an amphoteric starch which contains a cationic component and an anionic phosphate component and is made by;

(12) a) impregnating a cationic starch with a phosphate reagent to form an impregnated starch;

(13) b) drying the impregnated starch to substantially anhydrous conditions; and

(14) c) heating to phosphorylate the starch.

(15) A preferred embodiment involves the above process wherein the drying and phosphorylation take place in the fluidized state.

(16) DETAILED DESCRIPTION OF THE INVENTION

(17) This invention involves the use of specially prepared amphoteric starches in papermaking. The use of amphoteric starch additives in papermaking has long been known, as noted above, however, amphoteric starches containing a phosphate component and specifically prepared as described herein, have improved characteristics which make them especially useful in papermaking. These amphoteric starches are prepared in a process that has improved reaction efficiency and provides a product with high levels of substitution, particularly bound phosphorus, and minimum amounts of residual salts and other impurities. Such products are also characterized by improved properties such as viscosity, color and uniformity and have been found especially useful as wet end additives in papermaking.

(18) The amphoteric starches as used in this invention contain a cationic functional group and an anionic phosphate functional group and are prepared by impregnating a cationic starch with phosphate and then drying it to substantially anhydrous conditions, preferably when in the fluidized state, before heat treating to effect phosphorylation. By anhydrous or substantially anhydrous conditions is meant less than about 1% moisture content by weight, based on the dry weight of starch. It is preferred that both the drying and phosphorylation steps take place in the fluidized state. While other drying and phosphorylating systems may be used which are not in the fluidized state, the fluidized state is preferred because it provides excellent heat and mass transfer which results in good and desired drying and reaction characteristics.

(19) Impregnation by the phosphate reagent may be accomplished by adding the reagent, at a level of less than about 15% and preferably less than about 10% by weight of starch, either in the dry state or to the wet starch, or by dissolving the reagent in water to form an aqueous solution which is then mixed with the starch. These impregnation techniques are described in U.S. Pat. No. 4,166,173 issued Aug. 28, 1979 to O. Wurzburg et al. and U.S. Pat. No. 4,216,310 issued Aug. 5, 1980 to O. Wurzburg et al., both of which are incorporated herein by reference.

(20) The impregnated starch is first subjected to the fluidized

state and dried to anhydrous conditions of less than about 1% by weight moisture content, based on the weight of dry starch, at less than about 140.degree. C., more particularly between about 60 to 140.degree. C. and preferably between about 100 to 125.degree. C. The dried product, while still in the fluidized state, is heated to between about 100 to 185.degree. C., preferably between about 120 to 140.degree. C. for about 30 to 300 minutes. At temperatures higher than about 150.degree. C., the processing time is preferably less than about 45 minutes. Though the heat treatment may be carried out in one step, it is preferably carried out in two steps. When using a one step procedure, once reaction temperature is reached, anhydrous conditions have already or substantially been reached. The important point is that in either the one or two step operation, anhydrous conditions are reached before or in the very early stage of phosphorylation.

(21) The fluidized state is achieved by vigorous mixing of the solid starch particles in vacuum or in a gas whereby a uniform distribution of starch throughout the vacuum or gas may be attained. Vigorous mixing may be accomplished by using air or gas, at or above atmospheric pressures in a fluidized bed reactor or by sufficient mechanical agitation. Where pressurized gas is used to effect the fluidized state, the velocity of the gas must achieve a minimum rate such that the particles are free to move and exhibit a "fluidized state". The fluidized state results in very efficient heat transfer and allows the starch to rapidly dry to a virtually anhydrous state at low temperature.

(22) The phosphate esters prepared by predrying to anhydrous conditions while in the fluidized state as described above are characterized by improved purity as the high reaction efficiency provides a product with a high level of substitution while providing a low level of residual inorganic phosphate salts in the final amphoteric starch product. Further, the process minimizes side reactions such as starch hydrolysis and crosslinking. Such products are also characterized by improved viscosity, color and uniformity. The new process also preserves the granular integrity of the starch, advantageously allowing the optional washing of the final product.

(23) The amphoteric starch prepared as described above using anhydrous conditions and the fluidized state involves a process having improved reaction efficiency. Reaction efficiency is defined to be the amount of bound phosphorus divided by the total amount of phosphorus used in the process, multiplied by 100. Reaction efficiencies of this process may be as high as about 70 to 85% or more, and are much improved over the reaction efficiency of traditional methods of phosphorylating starches.

(24) The process of preparing starch phosphates and cationically modified starch phosphates (amphoteric starches) by impregnating

starch and cationic starch with a phosphate reagent and then drying to anhydrous conditions while in a fluidized state prior to heat treating is described in further detail in co-pending U.S. application Ser. No. 09/633,832 filed Aug. 7, 2000, entitled "Improved Starch Phosphate Ester Composition, Process and Method of Use in Food", with Wolfgang Bindzus et al. as inventors. The process, details of this process and compositions as described in U.S. application Ser. No. 09/633,832 are hereby incorporated herein by reference.

(25) The starch which may be used as the base material in preparing the amphoteric starch materials of this invention may be derived from any plant source including corn, potato, wheat, rice, tapioca, sago, sorghum, waxy varieties such as waxy maize and waxy rice, and high amylose varieties such as high amylose corn. Starch flours may also be used. Preferred starches are waxy maize, corn, tapioca, potato starch and combinations thereof. The term "waxy" as used herein is intended to include a starch or flour containing at least about 95% by weight of amylopectin and the term "high amylose" is intended to include a starch or flour containing at least about 40% by weight of amylose, preferably at least about 65% by weight of amylose.

(26) Also included as the base starch material are the conversion products derived from any of the former bases including, for example, dextrins prepared by hydrolytic action of acid and/or heat; oxidized starches prepared by treatment with oxidants such as sodium hypochlorite; fluidity or thin-boiling starches prepared by enzyme conversion or mild acid hydrolysis; derivatized or modified starches; and crosslinked starches. The starch base may be granular or a gelatinized starch, i.e. non-granular starch.

(27) The amphoteric starches as used in this invention contain both a cationic functional group and an anionic functional group. Cationization of the starch which typically is done before phosphorylation is performed by well known chemical reactions with reagents containing amino, imino, ammonium, sulfonium and phosphonium groups as disclosed, for example, in "Cationic Starches" by D. B. Solarek in Modified Starches: Properties and Uses, Chapter 8, 1986, pp. 113-129 and in U.S. Pat. No. 4,119,487 issued Oct. 10, 1978 to M. Tessler. Such cationic derivatives include those containing nitrogen groups comprising primary, secondary, tertiary and quaternary amines and sulfonium and phosphonium groups attached through either ether or ester linkages. The preferred cationic derivatives are those containing the tertiary amino and quaternary ammonium ether groups.

(28) The general method for preparing starches containing tertiary amine groups, which method involves reacting starch under alkaline conditions with a dialkylaminoalkyl halide is described in U.S. Pat. No. 2,813,093 issued on Nov. 12, 1957 to C. Caldwell, et al.. Another method is disclosed in U.S. Pat. No. 4,675,394 issued on Jan. 23,

1987 to D. Solarek et al.. The primary and secondary amine starches may be prepared by reacting the starch aminoalkyl anhydrides, amino epoxides or halides, or the corresponding compounds containing aryl in addition to the alkyl groups.

(29) Quaternary ammonium groups may be introduced into the starch by suitable treatment of the tertiary aminoalkyl ether or starch, as described in the previously noted U.S. Pat. No. 2,813,093. Alternatively, quaternary groups may be introduced directly into the starch by treatment with the reaction product of an epihalohydrin and a tertiary amine or tertiary amine salt, to provide, for example, (3-trimethylammonium chloride)-2-hydroxypropyl ether substituent groups as disclosed in the noted U.S. Pat. No. 4,119,487. The above noted patents, i.e., '487, '093 and '394 are incorporated by herein by reference.

(30) The preparation of cationic sulfonium derivatives is described in U.S. Pat. No. 2,989,520 issued June, 1961 to M. Rutenberg et al., and essentially involves the reaction of starch in an aqueous alkaline medium with a beta-halo-genoalkylsulfonium salt, vinylsulfonium salt or epoxyalkylsulfonium salt. The preparation of cationic phosphonium derivatives is disclosed in U.S. Pat. No. 3,077,469 issued Feb. 12, 1963 to A. Aszalos and involves reaction of starch in an aqueous alkaline medium with a beta-halogenoalkylphosphonium salt.

(31) Other suitable cationic salts may be provided using reagents and methods that are well known in the art as illustrated in the above references. Further description of useful cationic starches are disclosed in U.S. Pat. No. 2,876,217 issued Mar. 3, 1959 to E. Paschall, U.S. Pat. No. 2,970,140 issued Jan. 31, 1961 to C. Hullinger et al., U.S. Pat. No. 5,004,808 issued Apr. 2, 1991 to M. Yalpani et al., U.S. Pat. No. 5,093,159 issued Mar. 3, 1992 to J. Fernandez et al., and EP 406 837 published Jan. 1, 1991 (corresponding to U.S. application Ser. No. 516,024 filed Apr. 26, 1990), all of which are incorporated herein by reference. Particularly useful cationic derivatives are those containing amino or nitrogen groups having alkyl, aryl, aralkyl or cyclic substituents of up to 18 carbon atoms and especially alkyl of 1 to 6 carbon atoms.

(32) The amount of cationic substituent on the starch can be varied and generally a degree of substitution (DS) of from about 0.003 to 0.2 and preferably from about 0.01 to 0.1 will be used. While larger amounts of cationic substituents or higher degrees of substitution (DS) could be used, they are more costly and difficult to make and therefore not economically attractive. The term "degree of substitution" as used herein, means the average number of sites or substituent groups per anhydroglucose unit of the starch molecule.

(33) The anionic phosphate component of the amphoteric starch is

obtained by impregnating the cationic starch with phosphate reagent and then drying and heat treating as described above. "Phosphate reagent" as used herein is defined as any phosphate reagent used for phosphorylating starch including ortho-, pyro-, meta- or tripolyphosphates. Illustrative phosphate reagents are the alkali metal phosphates such as sodium and potassium ortho-phosphate, phosphoric acid, phosphorus oxychloride, sodium and potassium tripolyphosphate and sodium and potassium trimetaphosphate. The reagent may be either a mono-, di- or trialkyl metal phosphate or combinations thereof.

(34) Techniques for phosphorylating a starch base are further described in U.S. Pat. No. 2,824,870 issued Feb. 25, 1959 to H. Neukom and U.S. Pat. No. 2,961,440 issued Nov. 22, 1960 to R. Kerr. These patents disclose techniques of heat reacting starch impregnated with a phosphate salt of an alkali metal, within a prescribed pH range. Previously noted U.S. Pat. 3,562,103 directed to starches containing anionic phosphate groups, discloses a method of phosphorylating starch which comprises forming an aqueous starch slurry at room temperature and adding a suitable concentration of phosphate reagent. Preferably, the pH is adjusted to between 4 and 6, although it is stated that a range of 4 to 11.5 may be used. The starch is filtered without washing and adjusted to a moisture level of about 20% or below, preferably from about 5 to 20% by weight, based on weight of dry starch, at a temperature of less than about 70.degree. C. The starch phosphate composition is then heated at a temperature of 100 to 160.degree. C. until the product has the desired level of anionic phosphate groups. The above noted '870, '440 and '103 patents are all incorporated by reference.

(35) In U.S. Pat. No. 4,166,173 issued Aug. 28, 1979 to O. B. Wurzburg et al., which disclosure is incorporated herein by reference, starch is phosphorylated by an improved pollution-free process which involves forming a concentrated reagent solution of alkali tripolyphosphate salt and impregnating therewith a starch cake containing no more than 45% by weight of moisture. Drying and thermally reacting the thus impregnated starch provides the phosphorylated starch. In preparing the concentrated reagent solution, during addition of the tripolyphosphate salt to the water, one or more acids are added to control the pH at between 2.8 and 5.0.

(36) The amount of phosphorylating reagent used will depend on the reagent and is selected so that the resultant starch derivative contains about 0.03 to 1.0% of bound phosphorus and preferably about 0.1 to 0.5%. By the term "bound phosphorus" we mean phosphorus which is attached by an ester linkage to a hydroxyl group of the anhydroglucose backbone of the derivatized starch. Bound phosphorus may also be defined as the phosphorus that cannot be removed from the product by conventional washing or separation techniques.



(37) Most commonly, the amount of phosphorylating reagent employed will range from about 0.5 to 12% by weight of dry starch.

(38) The amphoteric starch derivative of this invention may be effectively used for addition to pulp prepared from any type of cellulosic fibers, synthetic fibers, or combinations thereof. Among the cellulosic materials which may be used are bleached and unbleached sulfate (kraft), bleached and unbleached sulfite, bleached and unbleached soda, neutral sulfite, semi-chemical, chemiground wood, ground wood or any combination of these fibers. Fibers of the viscose rayon or regenerated cellulose type may also be used if desired.

(39) Any desired inert mineral fillers may be added to the pulp which is to be modified with the improved amphoteric starch derivatives of this invention. Such materials include clay, titanium dioxide, talc, calcium carbonate, calcium sulfatae and diatomaceous earths.

(40) Other addidtives commonly introduced into paper may be added to the pulp or furnish, for example, dyes, pigments, sizing additives, alum, anionic retention aids, etc..

(41) The amount of amphoteric starch derivative that may be added to the wet end or paper pulp will be an effective additive amount, especially effective to improve drainage and filler retention. More particularly, from about 0.05 to 10% of the amphoteric starch and preferably from about 0.1 to 2% by weight, based on the dry weight of the stock or furnish, may be used. The amphoteric starch derivatives are dispersed or solubilized prior to addition to the papermaking system. This may be accomplished by standard or known techniques such as batch cooking, jet cooking or steam injection cooking.

(42) In addition to the selected amphoteric starch derivatives and other components that may be included in the alkaline papermaking system as described above, colloidal inorganic minerals may be added to the system to form an alkaline microparticle system. Such microparticle systems may include colloidal silica or bentonite, and alum and may be incorporated into the system in amounts of at least 0.001% and more particularly from about 0.01 to 1% by weight, based on the weight of dry pulp. Further description of such microparticle materials may be found in U.S. Pat. No. 4,388,150 issued Jun. 14, 1983; U.S. Pat. No. 4,643,801 issued Feb. 17, 1987; U.S. Pat. No. 4,753,710 issued Jun. 28, 1988 and U.S. Pat. No. 4,913,775 issued Apr. 3, 1990; all of which are incorporated herein by reference.

#### **DETAILED DESCRIPTION:**

(1) The following examples will further illustrate the embodiments

of this invention. In these examples, all parts are given by weight and all temperatures in degrees Celsius unless otherwise noted.

(2) EXAMPLE 1

(3) A fluid bed processed amphoteric starch was prepared as follows. One thousand (1000) g (anhydrous weight) of cationic waxy corn starch (amylopectin-2-hydroxy-3-(trimethylammonium) propyl ether chloride, commercially available from National Starch and Chemical Company) was impregnated with 20 g (2%) sodium tripolyphosphate. The starch was slurried in 2500 g of water and the slurry pH was adjusted to 6 and stirred for 30 minutes. The starch slurry was filtered (de-watered) using a Buchner funnel and a vacuum flask and 154 g of a 13% aqueous solution was poured over the filter cake. This treatment resulted in impregnated starch having 0.51% of inorganic phosphorus tarch. The impregnated starch was air dried at about 25.degree. C. to a moisture content of about 10% and ground using a Prater mill. The heat treatment of the starch to affect the starch phosphorylation, was carried out in a fluid bed reactor using the following process conditions. First, the starch was dried at a temperature of about 104.degree. C. (220.degree. F.) until the moisture content was less than 1% by weightrds, the temperature was increased to 126.degree. C. (260.degree. F.) and the heat treatment carried out over 20 minutes. The heat treatment resulted in a level of bound phosphorus of 0.19% and the reaction efficiency was 38% (Sample A).

(4) The above fluid bed processed amphoteric starch (Sample A) was evaluated for drainage performance and compared to a conventionally prepared amphoteric starch (amylopectin-dihydrogen phosphate-2-hydroxy-3-(trimethylammonium) propyl ether-chloride-sodium salt, commercially available from National and Chemical Company) having a bound phosphorus of 0.18% (Sample B). The comparative sample was prepared by impregnating waxy corn starch with an aqueous sodium tripolyphosphate solution using a method described in U.S. Pat. No. 4,216.310. The impregnation resulted in 0.85% of inorganic phosphorus on starch. This phosphorus usage level was significantly higher than for Sample A. After impregnation, the moisture content of the starch was about 4%. The phosphorylation reaction was carried out by heat treating the starch for about 45 minutes in a continuous cooker. The heat treatment resulted in a level of bound phosphorus of 0.18% with a reaction efficiency of 22% (Sample B). The drainage performance was determined using a dynamic drainage jar. The paper pulp which was used for this test was adjusted to a pH of 5.5. The two starch samples were water bath cooked at 1% solids and the amount of starch which was added to the paper pulp corresponded to addition levels of 8 and 20 lbs of starch per ton of paper. The results are given in Table 1 and show very similar drainage performance for samples A and B. This indicates that the fluid bed prepared amphoteric waxy corn starch is very suitable and functional as a drainage aid in the wet end of papermaking. The advantage of this fluid bed process is that

it is possible to make functional amphoteric starches using a reduced amount of phosphate reagent due to improved reaction efficiency.

(1) TABLE 1 Drainage Performance of Amphoteric Waxy Corn Starches  
 Drainage Performance Test Sample 8 lbs starch/ton paper 20 lbs  
starch/ton paper (ml/s) ml/s Sample A 98 234 Sample B 99 232

(5) EXAMPLE 2

(6) A fluid bed processed amphoteric starch was prepared as follows. A 1000 g (anhydrous weight) amount of cationic waxy corn starch (described in Example 1) was impregnated with 2% (20 g) of sodium tripolyphosphate. The starch was slurried in 2500 g of water and the slurry pH was adjusted to a level of 6 and stirred for 30 minutes. The starch slurry was filtered (de-watered) using a Buchner funnel and a vacuum flask and 154 g of a 13% aqueous sodium tripolyphosphate solution was poured over the filter cake. This treatment level resulted in 1.04% inorganic phosphorus on starch. The impregnated starch was air dried at about 25.degree. C. to a moisture content of about 10% and ground using a Prater mill. The heat treatment of the impregnated starch, which affects the starch phosphorylation, was carried out in a fluid bed reactor using the following reaction conditions. First the starch was dried at a temperature of 104.degree. C. (220.degree. F.) until the moisture was less than 1%. Afterwards, the temperature was increased to 116.degree. C. (240.degree. F.) and the heat treatment was carried out for 100 minutes. The heat treatment resulted in a level of bound phosphorus of 0.286%. The fluid bed processed amphoteric starch (Sample C) was evaluated for drainage performance and compared to a conventionally prepared amphoteric similar to the one prepared in Example 1 (Sample D). Sample D had an impregnation of 0.72% of inorganic phosphorus on starch. After impregnation, the moisture content of the starch was about 4%. The phosphorylation reaction was carried out by heat treating the starch for about 45 minutes in a continuous cooker. The heat treatment resulted in a level of bound phosphorus of 0.168%.

(7) The drainage performance was determined using a dynamic drainage jar. The paper pulp which was used for this test was adjusted to a pH of 5.8. The amount of starch which was added to the paper pulp corresponded to addition levels of 10 to 40 lbs starch per ton of paper. The results are given in Table 2 and showed that the use of the fluid bed processed amphoteric starch (Sample C) gave significantly improved drainage performance.

(2) TABLE 2 Drainage Performance of Amphoteric Waxy Corn Starch  
Starch Addition Drainage Performance (cc/sec) lbs/T Sample C Sample D  
 10 183 156 20 234 176 30 268 211 40 259 217

(8) EXAMPLE 3

(9) An amphoteric waxy corn starch was prepared as follows. Cationic waxy corn starch (described in Example 1) was impregnated with an aqueous sodium tripolyphosphate solution and dried to a moisture content of about 8%. The impregnation resulted in 0.706% phosphorus on starch as determined via inductively couple plasma analysis. The starch phosphorylation was carried out in a Processall reactor under sufficient agitation to fluidized the product. After the starch was loaded into the reactor, it was agitated at about 150 rpm to obtain conditions comparable to a fluidized state. The starch was dried at a temperature of about 121.degree. C. (250.degree. F.) until the moisture was less than 1%. Vacuum was applied in order to improve the drying process. Once the moisture was less than 1%, the temperature was increased to a reaction of 143.degree. C. (290.degree. F.) and samples were taken once the temperature reached 143.degree. C. (Sample E) and after the heat treatment was carried out for 60 minutes (Sample F). The heat treatment resulted in levels of bound phosphorus of 0.21% (Sample E) and 0.27% (Sample F). These sample (E and F) together with a comparative conventionally prepared amphoteric starch (Sample B) used in Example 1, were evaluated for drainage performance in paper pulp under acidic conditions following the procedure described in Example 1. The results are given in Table 3 and indicate that drainage performance is significantly better for Sample F over the comparative Sample B while the drainage performance of Sample E was slightly improved over the comparative Sample B.

(3) TABLE 3 Drainage Performance of Amphoteric Waxy Corn Starch  
Starch Addition Drainage Performance (cc/sec) Lbs/ton paper Sample E  
 Sample F Sample B 10 156 153 149 20 174 187 172 30 181 205 176 40 187  
 211 181

(10) The samples described above were further evaluated for filler retention performance. The evaluation was carried out in an alkaline papermaking system using Dynamic Alkaline Retention Evaluation, Tappi 261 pm 90 in an alkaline paper system (pH 7.8). A standard papermaking furnish was prepared using a pulp stock which comprised an aqueous slurry of bleached hardwood kraft paper and bleached softwood kraft pulp. The pulp stock was refined in an aqueous solution to about 400 Canadian Standard Freeness (CSF) and a pH of 7.7 to 8.2 and contained precipitated calcium carbonate filler (30% db) with 8 to 10% fiber fines and total fines of 37 to 42%. The test was run while mixing and agitating using a Brift jar with a screen having holes 76 microns in diameter. The results are given in Table 4 below. The filler retention for Sample E was 23.6% CaCO<sub>3</sub> at a starch addition level of 10 lbs per ton of paper and increased to 57.7% CaCO<sub>3</sub> at an addition level of 40 lbs per ton of paper. Sample F also showed an increase from 23.1 to 49.9% CaCO<sub>3</sub> as the additional level was increased from 10 to 40 lbs per ton of paper. The filler retention of Sample E matched the performance of standard Sample B while that of Sample F was slightly less.

(4) TABLE 4 Retention Performance of Amphoteric Waxy Corn Starch  
Starch Addition Retention Performance (% CaCO.sub.3) Lbs/ton paper  
Sample E Sample F Sample B 10 23.6 23.1 28.0 20 40.3 34.1 42.7 30  
49.8 42.3 49.5 40 57.7 49.5 57.5

**CLAIMS:**

What is claimed is:

1. A method of making paper comprising adding to the paper stock prior to or during formation of the sheet, an effective amount of an amphoteric starch which contains a cationic component and an anionic phosphate component and is made by:

a) impregnating a cationic starch with a phosphate reagent to form an impregnated starch;

b) drying the impregnated starch to a moisture content of less than 1% by weight of starch; and

c) heating to phosphorylate the starch.

2. The method of claim 1 wherein the starch is waxy maize, corn, tapioca, potato starch or a combination thereof.

3. The method of claim 2 wherein the phosphate reagent is an alkali metal ortho-, pyro-, meta-, or tripolyphosphate.

4. The method of claim 3 wherein the cationic component is a tertiary amino or quaternary ammonium ether group.

5. The method of claim 1 wherein the impregnated starch is dried and phosphorylated while in the fluidized state.

6. The method of claim 5 wherein the starch is waxy maize, corn, tapioca, potato starch or a combination thereof.

7. The method of claim 6 wherein the phosphate reagent is an alkali metal ortho-, pyro-, meta-, or tripolyphosphate.

8. The method of claim 7 wherein the cationic component is a tertiary amino or quaternary ammonium ether group.

9. The method of claim 8 wherein from about 0.05 to 10% by weight of the amphoteric starch, based on the dry weight of the paper stock, is used.

10. The method of claim 9 wherein from about 0.5 to 12% by weight of phosphate reagent, based on the weight of dry starch, is used.

11. The method of claim 9 wherein the amphoteric starch contains about 0.03 to 1% of bound phosphorus.

12. The method of claim 8 wherein from about 0.1 to 2% by weight of the amphoteric starch, based on the dry weight of the paper stock is used and it contains from about 0.1 to 0.5% bound phosphorus.

13. The method of claim 12 wherein the impregnated starch is dried while in the fluidized state at a temperature of less than about 140.degree. C.

14. The method of claim 13 wherein the temperature is from about 60 to 140.degree. C.

15. The method of claim 12 wherein the starch is phosphorylated by heating to a temperature of between about 100 to 185.degree. C.

16. The method of claim 14 wherein the starch is phosphorylated by heating to a temperature of between about 120 to 140.degree. C.

17. Paper made by the method of claim 1.

18. Paper made by the method of claim 4.

19. Paper made by the method of claim 5.

20. Paper made by the method of claim 12.

21. Paper made by the method of claim 16.

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**DOCUMENT-IDENTIFIER:** US 6248338 B1  
**TITLE:** Starchy cleaning and cosmetic care preparations  
**DATE-ISSUED:** June 19, 2001

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**SEARCH:** 424/70.13 ; 514/778 ; 514/844 ; 514/944 ; 510/109

**REF-CITED:**

**U.S. PATENT DOCUMENTS**

| <b>PAT-NO</b>  | <b>ISSUE-DATE</b> | <b>PATENTEE-NAME</b> | <b>US-CL</b>   |         |
|----------------|-------------------|----------------------|----------------|---------|
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**FOREIGN PATENT DOCUMENTS**

| <b>FOREIGN-PAT-NO</b> | <b>PUBN-DATE</b> | <b>COUNTRY</b> | <b>US-CL</b> |
|-----------------------|------------------|----------------|--------------|
| 249 912               | September 1987   | DE             |              |
| 55-127308             | October 1980     | JP             |              |
| 56-147622             | November 1981    | JP             |              |
| 63-62535              | March 1988       | JP             |              |
| 92066778              | April 1992       | WO             |              |

**OTHER PUBLICATIONS** R.E. Faust, "Starches in Topical Preparations", American Perfumer and Cosmetics, vol. 78, Oct. 1963, pp. 51-54.

**ART-UNIT:** 166  
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**ABSTRACT:**

A composition for cleaning or caring for the skin, teeth or hair



or for cleaning smooth surfaces in described, which has an aqueous phase containing a pregelatinized, crosslinked starch selected from a C.sub.2 -C.sub.5 hydroxyalkyl starch and a C.sub.2 -C.sub.18 acyl starch. Preference is given to hydroxypropyl di-starch phosphate or di-starch C.sub.4 -C.sub.18 -alkanoate or alkenoate. The starch acts 1) as a stability improver, 2) as a viscosity regulator, 3) as a (co) emulsifier, 4) as a skin feel improving agent and 5) as an agent for improving hairdressing characteristics.

28 Claims, 0 Drawing figures

Exemplary Claim Number: 1

#### **BRIEF SUMMARY:**

##### (1) BACKGROUND OF THE INVENTION

(2) The present invention relates to compositions for cleaning or caring for the skin, teeth or hair, as well as for cleaning smooth surfaces. Consequently the invention relates to compositions which are intended to come or can come in contact with human skin.

(3) Humectant characteristics, tactile characteristics giving a soft feel to the skin and lips, and a smooth, easily spreadable texture are sought in cosmetics. In conventional cosmetic compositions the tactile characteristics are provided by hydrophobic constituents such as waxes, oils and fats.

(4) Improved humectant characteristics are obtained by adding to the composition hydrophilic constituents and forming a stable water-in-oil emulsion. The prior art emulsion-like compositions suffer from various disadvantages, e.g., lack of emulsion stability and high ingredient costs (e.g., hyaluronic acid), particularly in cream, lotion and beauty soap compositions.

(5) The prior art discloses cosmetics which contain certain starches for overcoming these disadvantages.

(6) U.S. Pat. No. 5,279,313 describes a hair bleaching composition which contains a persulphate having a specific particle size and alkaline reacting salts. As water-soluble thickeners, the composition can contain starches. Examples include maize or corn starch, starch ethers, such as carboxymethyl starch, hydroxyethyl starch and ethyl starch. The products according to U.S. Pat. No. 5,279,313 do not have adequate viscosity, storage stability and use characteristics.

(7) JP 63-62535 describes the production of a stabilizing emulsifier, for whose production lecithin and polyglycerol are emulsified in a starch hydrolyzate solution and modified starch and

xanthan gum are added. The modified starch is e.g. hydroxypropyl di-starch phosphate, hydroxypropyl starch or di-starch phosphate. The emulsifier obtained is intended to be a gum Arabic replacement. The fields of use given are condiments, emulsified spices, flavours, pastries, dairy products and medicinals. JP 63-62535 contains no information regarding a possible use in cosmetic or cleaning compositions. The starches used in the examples are cooking starches.

(8) U.S. Pat. No. 4,059,458 relates to oil-in-water emulsions for use in foods, pharmaceuticals and cosmetics which contain an ester of a starch with at least one aliphatic C.sub.2 -C.sub.4 carboxylic acid. The ester has a degree of substitution of 0.05 to 1.0 and can optionally be modified, oxidized, crosslinked or pregelatinized. The starch esters are not hydrolysis-stable, particularly in formulations having an acidic pH. This leads to an undesired viscosity drop, phase separation and an unpleasant odor caused by free carboxylic acids.

(9) WO 92/06778 discloses compositions containing a C.sub.12 - C.sub.22 alcohol, an alkyl polyoside and optionally polyoside. The alkyl polyoside can inter alia incorporate glucose, saccharose, maltose, lactose, cellobiose and starch. The compositions are intended for use in cosmetics and pharmaceuticals.

(10) WO 93/04185 describes the enzymatic, stereospecific preparation of alpha-glucosides from starch, maltodextrin or maltose. The alpha-glucosides can be further reacted in the presence of a lipase with a fatty acid, in which alpha-glucoside esters are obtained which are suitable as detergents, surfactants and emulsifiers in cosmetic or pharmaceutical compositions. The starch merely serves as a reservoir for glucose units and is decomposed to low molecular weight units.

(11) DD 249 912 discloses starch derivatives which are prepared by etherifying a starch with a halogenated fatty acid and heating to 80 to 130.degree. C. to form intermolecular ester bridges. The starch derivatives are suitable as emulsion stabilizers in the pharmaceutical, cosmetic and foods industries. These products are not suitable for building up an increased viscosity.

(12) JP 56-147622 describes an emulsifier composition which contains the monoesters of a fatty acid with a trihydric alcohol, as well as galactomannan, glucomannan and/or starch.

(13) JP 55-127308 describes weak acid, emulsified cosmetics which contain an oil-like cosmetic material, cationic cellulose or cationic starch with a specific N-content, triethanol amine or triisopropanol amine, higher fatty acids and water.

(14) The known starch-containing cosmetics and cleaning

compositions suffer from numerous disadvantages. In cold water native starch is a insoluble biopolymer. Thus, when using native starch it is necessary to heat over a long time period when producing the composition in order to solubilize the starch. In addition, agglomeration can occur when the starch is incorporated in water or an aqueous base. Apart from these processing disadvantages, the known starch-containing products have disadvantages during use and e.g. have an unpleasant, sticky feel on the skin or undissolved particles give an unpleasant, rough feeling. In addition, problems can occur in connection with the storage stability, which can be manifested in a phase separation, retrogradation of the starch used or lack of odor stability.

(15) Therefore, the problem to be solved by the invention is to provide starch-based compositions which do not suffer from the aforementioned disadvantages.

(16) SUMMARY OF THE INVENTION

(17) According to the invention, this problem is solved by a composition for cleaning or caring for the skin, teeth or hair or for cleaning smooth surfaces comprising an aqueous phase which contains a pregelatinized, crosslinked starch selected from a C.sub.2 -C.sub.5 hydroxyalkyl starch and a C.sub.2 -C.sub.18 acyl starch.

(18) The starch to be used according to the invention must be crosslinked. Crosslinking of the starch chains can be achieved by suitable crosslinking agents, i.e., bifunctional compounds. A preferred crosslinking method is phosphorylation, in which the starch is reacted with phosphorous oxychloride, phosphorous pentoxide, and/or sodium trimetaphosphate. Two starch chains are crosslinked by an anionic P-O group. The anionic character of the crosslinking sites assists the emulsion-stabilizing action of the starch to be used according to the invention. A further preferred crosslinking method is by means of C.sub.4 -C.sub.18 alkane or alkene dicarboxylic acids, preferably C.sub.4 -C.sub.8 alkane dicarboxylic acids, and in particular adipic acid. The alkane or alkene dicarboxylic acid links two starch chains via ester bonds. It can be in straight or branched chain form. The derivatives are obtained, e.g., by reacting starch with the mixed anhydrides of dicarboxylic acid and acetic acid. Based on the dry starch, in general less than 0.1 wt. %, normally about 0.06 wt. %, crosslinking agent is used.

(19) The nature of the modification of the starch to be used according to the invention is critical. In one embodiment, the starch is C.sub.2 -C.sub.5 hydroxyalkyl starch. It is assumed that the formation of a hydroxyl group, which is bound to the starch backbone via an alkyl group with 2 to 5 carbon atoms, leads to a suitable hydrophilic-lipophilic balance of the starch. The position of the hydroxyl group in the alkyl group is not critical and can be in the

alpha to omega position. The degree of substitution of the hydroxyalkylation is preferably approximately 0.08 to 0.3. The degree of substitution is the average number of substituted OH groups of the starch molecule per anhydroglucose unit. The hydroxyalkylation of a native starch can be brought about by reacting a native starch with alkylene oxides with the appropriate number of carbon atoms. Particularly preferred are hydroxyethylated and/or hydroxypropylated starches obtained by reacting starches with ethylene oxide or propylene oxide. A starch to be used according to the invention can also contain more than one hydroxyl group per alkyl group.

(20) In another embodiment the starch is a C.sub.2 -C.sub.18 acyl starch. This starch regularly occurs if the aforementioned essential crosslinking has been brought about by C.sub.4 -C.sub.18 alkanolate or alkenolate and can be additionally acylated with a view to a suitable hydrophilic-lipophilic balance with a degree of substitution of 0 to 0.8, particularly 0 to 0.5. Acylation generally takes place by reaction with acid anhydrides of general formula (R--C(O)).sub.2 O, in which R is an alkyl group, such as methyl or ethyl, with succinic or maleic anhydride or their alkylated derivatives.

(21) A particularly preferred starch derivative for the purpose of the invention is a hydroxypropyl di-starch phosphate, as well as acetylated di-starch adipate.

(22) The starch starting material can be derived from any plant source, but preferably the starch has an amylopectin content of at least about 70 wt. %, preferably about 85 wt. %, and in particular about 90 wt. %. Particularly preferred starches are derived from waxy maize.

(23) A decisive feature of the invention is that the starch derivative to be used according to the invention is pregelatinized. Apart from the term "pregelatinized starch" the prior art also uses the terms "prepasted starch" and "cold water swelling starch". The term "pregelatinized" or "gelatinized" starch relates to swollen starch particles, which have lost their birefringence crosses in polarized light. Pregelatinized starches or starch derivatives are soluble in cold water without cooking. In this context "soluble" does not necessarily mean the formation of a true molecular solution and instead usually a colloidal dispersion is obtained. The starch derivative to be used according to the invention is preferably completely pregelatinized.

(24) The process normally used for producing such pregelatinized starches are inter alia drum drying, extrusion and spray drying.

(25) Drum drying includes the simultaneous cooking and drying of a very high viscosity, semi-solid starch paste on heated drums. The dried films are stripped from the drum with a metal blade and then

ground. This process can be carried out up to a very high solids content.

(26) It is also possible to use extrusion for the simultaneous cooking and drying of starches (cf. U.S. Pat. No. 3,137,592). This process makes use of the physical processing of a starch/water mixture at elevated temperatures and pressures which brings about the gelatinization of the starch, followed by expansion after leaving the nozzle with sudden evaporation of the water.

(27) The use of pregelatinized starch derivative allows the production of the composition according to the invention at ambient temperature or at a temperature which is considerably lower than the production conditions used for known starch-containing compositions. It has surprisingly been found that with a cooking starch (i.e., non-gelatinized starch) modified in the same way as a starch to be used according to the invention, the desired advantages regarding rheology, skin feel and emulsion stability are not obtained even if the aqueous phase, following addition of the cooking starch, is heated for 15 minutes to a temperature above the gelatinizing temperature of the starch.

(28) Preferably, the pregelatinized starch derivative is produced by spray drying. In other drying processes, e.g., drum drying, starch crusts can be formed which have an inferior solubility. This leads to undissolved particles in the composition according to the invention, which can give rise to an unpleasant, sandy feel on the skin.

(29) Preferably, the starch derivative to be used according to the invention has a majority of intact starch granules. It has been found that the aqueous dispersions of pregelatinized starch derivatives having a largely intact granular structure have a more uniform smooth texture than aqueous dispersions of starches without a granular structure, which are, e.g., obtained by drying starch solutions whose dispersions have a slightly gritty feel. In the case of pregelatinized starches with an intact granular structure the native internal structure of the hydrogen bonds is destroyed, but the external shape or form is maintained.

(30) A process for producing particularly suitable, spray dried, pregelatinized starches or starch derivatives is described in U.S. Pat. No. 4,280,851. An apparatus adapted for carrying out the process is described in U.S. Pat. No. 4,600,472. In this process a mixture of the granular starch or starch derivative is cooked or gelatinized in the atomized state. The starch to be cooked is atomized through an atomizing opening into a nozzle arrangement in order to form a relatively finely divided sprayed material. In addition, a heating medium is injected through an opening in the nozzle arrangement into the sprayed material so as to heat the starch to the temperature necessary for gelatinization. A closed chamber surrounds the

injection openings for the atomizing and heating medium and defines a ventilation opening positioned in such a way that the heated starch spray material can leave the chamber. The arrangement is such that during the passage of the starch spray material through the chamber, i.e., from the atomizing opening to the ventilation opening, the time elapsed defines the starch's gelatinization time. The resulting spray dried, pregelatinized starch includes uniformly gelatinized starch granules in the form of indented spheres, most of the granules being whole and unbroken and swollen after hydration. Nozzles usable for producing such starches are also described in U.S. Pat. No. 4,610,760.

(31) For the production of suitable pregelatinized starches or starch derivatives it is also possible to use the process of U.S. Pat. No. 5,149,799. In this process starch is uniformly atomized and cooked by means of a single atomization stage in the presence of an aqueous medium. The atomization stage is performed in an apparatus having an internal mix two-fluid spray drying nozzle and it is coupled to a device for drying the cooked, atomized starch.

(32) Spray dried, pregelatinized starches or starch derivatives with suitable characteristics can also be produced by a continuous, coupled jet-cooking and spray-drying process. A starch suspension is gelatinized at 138 to 160.degree. C. in a jet cooker with direct steam injection. The streams of starch suspension and steam are mixed in a cooking or boiling chamber. The outlet of the latter is connected to a pneumatic spray nozzle or a high pressure nozzle, which is located in a conventional spray dryer. The jet-cooked starch is directed at elevated temperature and pressure into the spray nozzle and can be atomized with cold air, hot air or preferably steam. After atomizing, the hot, jet-cooked starch solution is handled in the same way as conventional spray dried starches. The drying process is adequately fast to prevent retrogradation of the starch molecules during the cooling and drying of the droplets. The spray dried starch is an amorphous material (i.e., it is substantially non-crystalline) which is easily soluble in water or colloiddally dispersible.

(33) The composition according to the invention can be provided in any form, for example, as solution, emulsion, suspension, gel or foam. It can also be provided as a dry powdery composition which is reconstituted in an aqueous medium upon use. In general, the composition has preferably about 5 to 98%, particularly about 50 to 90 wt. %, of an aqueous phase. The aqueous phase preferably contains about 0.1 to 20 wt. %, particularly about 0.3 to 12 wt. %, and in a particularly preferred manner about 0.5 to 7 wt. %, of the starch derivative with the aforementioned features. The starch derivative to be used according to the invention can be used in conjunction with other starches, such as native starches, modified starches, and like starches.

(34) In the composition according to the invention the inventively used starch derivative fulfils various functions. It acts 1) as a stability improver, 2) as a viscosity regulator, 3) as a (co) emulsifier, 4) as an agent for improving the skin feel, and 5) as an agent for improving hairdressing characteristics.

(35) Aqueous dispersions of such starch derivatives are characterized by a variety of fat-like textures, which can range from oily, via creamy to waxy. These starch derivatives can be chosen in such a way that in aqueous dispersions starch gels of high strength or heat-reversible starch gels are obtained. A heat-reversible starch gel melts on heating and re-forms after cooling. Gels produced from unmodified starches are not heat-reversible. With the starches to be used according to the invention it is possible to wholly or partly replace oil or fat, and e.g., formulate oil-free lotions which have similar properties to oil-in-water emulsions.

(36) The starch derivatives to be used according to the invention have use characteristics which are desirable from the dermatological standpoint. They increase the water retention capacity of the skin and make the latter smooth and flexible. Cosmetics containing a starch derivative to be used according to the invention can be spread very well onto the skin and do not leave behind a sticky feeling.

(37) The starch derivatives to be used according to the invention have a stabilizing and oil-binding effect. They prevent the deposition of solid constituents, as well as the phase separation of liquid constituents. They also have a viscosity-raising effect and give the inventive composition a pleasing gloss. The starch derivatives to be used according to the invention also have a certain protective colloid action and consequently prevent the coalescing of emulsified droplets of a hydrophobic phase. Due to their action as a (co)emulsifier, it is possible to reduce the quantity of surface-active emulsifiers in the inventive cosmetics compared with conventional cosmetics. In certain cases there is no need for surface-active emulsifiers. Compared with other products, this offers advantages in cosmetics whose "natural" and "hyperallergenic" properties are stressed. The starch derivatives to be used according to the invention also have substantive characteristics, i.e., they can be drawn onto the human hair and make the latter more easily combable and sleek.

(38) The oil-binding characteristics of the starch derivatives to be used according to the invention lead to an improved transport of oil-soluble active ingredients of the inventive cosmetics on the skin surface.

(39) DESCRIPTION OF THE PREFERRED EMBODIMENTS

(40) In a preferred embodiment the composition according to the

invention contains at least about 0.3%, preferably about 7 to 25%, and in individual cases up to 70 wt. % surfactants. These compositions are in particular those in which a cleaning action is essential, e.g., shampoo, shower gel, foam bath, liquid soap, manual dishwashing composition or hair conditioning composition. Hereinafter these compositions are collectively referred to as WAS/starch combinations (WAS refers to washing-active substances).

(41) The surfactants are preferably anionic, amphoteric and/or nonionic surfactants. Suitable anionic surfactants include alkali metal salts of alkyl sulfonates or sulfates with 8 to 22 carbon atoms in the alkyl chain. Sodium, ammonium, potassium or triethanol amine alkyl sulfates are preferred, particularly those obtained by the sulfation of higher alcohols (8 to 18 carbon atoms), as well as sodium salts of coconut oil fatty acid monoglyceride sulfates or sulfonates, sodium or potassium salts of sulphuric acid esters of adducts of 1 to 12 mole of ethylene oxide to higher fatty alcohols (e.g. tallow or coconut oil alcohols), sodium or potassium salts of alkyl phenol-ethylene oxide-ether sulfates with 1 to 10 ethylene oxide units per molecule, in which the alkyl radicals contain 8 to 12 carbon atoms, sodium alkyl glyceryl ether sulfonates, reaction products of C.sub.10 to C.sub.22 fatty acids, esterified with isethionic acid, sodium salt, water-soluble salts of condensation products of fatty acids with sarcosine. Further anionic surfactants are sulfoacetates and sulfosuccinates.

(42) As amphoteric surfactants reference can be made to those constituting derivatives of aliphatic, quaternary ammonium, phosphonium and sulphonium compounds, in which the aliphatic radicals can be straight or branched and one of the aliphatic substituents contains 8 to 18 carbon atoms and one anionic group, e.g. a carboxylate, sulfonate, sulfate, phosphate or phosphonate group. Examples of these are 4-[N,N-di(hydroxyethyl)-N-octadecylammonio]-butane-1-carboxylate, 5-S-hydroxypropyl-S-hexadecyl-sulfonio]-3-hydroxypentane-1-sulfate, 3-[P,P-diethyl-P-3,6,9-trioxatetra-dioxylphosphonio]-2-hydroxypropane-1-phosphate, 3-[N,N-dipropyl-N-3-dodecoxy-2-hydroxypropylammonio]-propane-1-phosphate, 3-(N,N-dimethyl-N-hexadecylammonio)-1-sulfonate, 3-(N,Ndimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate, 4-[N,N-di(2-hydroxyldodecyl-ammonio)-butane-1-carboxylate, 3-[S-ethyl-S-(3-dodecoxy-2-hydroxypropyl)-sulphonio]-propane-1-phosphate, 3-[P,P-dimethyl P-dodecyl-phosphonio]-propane-1-phosphonate and 5-[N,N-di(3-hydroxypropyl)-N-hexadecylammonio]-2-hydroxypentane-1-sulfate. Betaines are also suitable for the invention. Suitable betaines are inter alia the higher alkyl betaines, e.g. coconut dimethyl carboxymethyl betaine, lauryl dimethyl carboxymethyl betaine, lauryl dimethyl alpha-carboxyethyl betaine, cetyl dimethyl carboxymethyl methane, cetyl dimethyl carboxymethyl betaine, lauryl-bis(2-hydroxyethyl)-carboxymethyl betaine, stearyl-bis(2-hydroxypropyl)-carboxymethyl betaine, oleyl dimethyl-gamma-carboxypropyl betaine,



lauryl-bis(2-hydroxypropyl)-alpha-carboxyethyl betaine, etc., sulfobetaines, such as coconut dimethyl sulfopropyl betaine, stearyl dimethyl sulfopropyl betaine, lauryl dimethyl sulfoethyl betaine, lauryl-bis(2-hydroxyethyl)-sulfopropyl betaine, etc.; amido betaines and amidosulfo betaines, in which a  $\text{RCONH}(\text{CH}_2)_3$  radical is connected to the betaine nitrogen atom are also suitable.

(43) Nonionic surfactants, which are preferably used in combination with an anionic or amphoteric surfactant, can roughly be defined as compounds prepared by the condensation of an alkylene oxide on a hydrophobic organic compound. Examples of preferred classes of nonionic surfactants are polyethylene oxide condensates of alkyl phenols, e.g. the condensation products of alkyl phenols with 6 to 12 carbon atoms in the alkyl group with 10 to 60 mole ethylene oxide, condensation products of ethylene oxide with propylene oxide-ethylene diamine reaction products, condensation products of aliphatic alcohols with 8 to 18 carbon atoms with ethylene oxide, long-chain, tertiary amino oxides, long-chain, tertiary phosphine oxides, long-chain dialkyl sulfoxides. The term "long-chain" means that in the molecule there is at least one long hydrophobic chain which contains an alkyl, alkenyl, hydroxyalkyl or ketoalkyl radical with 8 to 20 carbon atoms. Other examples of nonionic surfactants are alkyl and alkenyl oligoglycosides, such as  $\text{C}_{12}$ - $\text{C}_{14}$  coconut alkyl oligoglucoside.

(44) For hair care compositions and hair conditioning compositions, usually cationic compounds, preferably quaternary ammonium compounds, such as cetyl trimethyl ammonium chloride or diquaternary polydimethyl siloxanes, are used. The starch derivative to be used according to the invention shows the benefit of being compatible with cationic compounds, i.e., it remains dispersed in the presence of the cationic compound and maintains its viscosity.

(45) The composition preferably has a pH-value between about 2.5 and 12, particularly between about 4 and 9. A desired pH-value is attained by adding suitable pH-regulators, such as citric acid, lactic acid, phosphoric acid, hydrochloric acid, sodium hydroxide, potassium hydroxide or triethanol amine. When using starch esters a strong acid pH-value should be avoided, because otherwise there is a hydrolysis of the ester bonds.

(46) In a further embodiment, the composition according to the invention contains at least about 1 wt. %, particularly about 5 to 25 wt. %, and in individual cases up to 70 wt. % of a hydrophobic phase. The hydrophobic phase is preferably finely dispersed. The hydrophobic phase can correspond to the hydrophobic phase of conventional oil-in-water-based cosmetics and, e.g., contains liquid or solid fatty acid triglycerides, fatty acid monoesters or diesters, silicones and/or long-chain alcohols. These compositions are collectively referred to hereinafter as "emulsion-type" compositions.

(47) To maintain the hydrophobic phase as fine dispersion, the emulsion-type compositions according to the invention preferably contain one or more additional emulsifiers, particularly a partial ester of a polyhydric alcohol, an ethoxylate, propoxylate and/or butoxylate having a HLB value of about 4 to 16 and/or ionic emulsifiers, such as citrates or tartrates of monoglycerides. It is also possible to use combinations of glycerin monostearate or distearate with fatty alcohol sulfates or alkali metal salts of fruit acid esters or glycerin mono- or difatty acid esters. The emulsifier is preferably about 0.1 to 10 and in particular about 0.5 to 5 wt. %. In this embodiment the inventive composition can be in the form of a cream, lotion or milk. As a function of the characteristics and quantity of the aqueous or hydrophobic phase, the emulsion-type compositions can contain different types of emulsions, e.g., binary oil-in-water or water-in-oil systems or multiple phase systems, such as water-in-oil-in-water or oil-in-water-in-oil systems.

(48) In another preferred embodiment, the composition according to the invention is in the form of a high viscosity gel. The gel according to the invention preferably contains one or more monohydric or polyhydric alcohols, with particular preference being given to glycerin and/or ethanol. In the gel the alcohol is preferably present in a quantity of about 5 to 25 wt. %. A quantity of 25 wt. % should not be exceeded because otherwise the starch can precipitate. The gel can contain agents which give the skin a refreshing and cooling effect, such as e.g., menthol or menthyl lactate.

(49) A further preferred embodiment of the invention is a hair dyeing or hair bleaching composition. These compositions are characterized by containing a colorant or an oxidizing agent, respectively. Generally, as oxidizing agents percompounds, such as peroxides, e.g., hydrogen peroxide, or persulfates are useful. The hair dyeing or hair bleaching composition can be provided as a one-component composition or preferably as a two-component composition. The two components of the composition are combined by the user prior to use and applied to the hair. If the composition is provided as two components, it is preferred that one component is powdery and the other component is liquid. The powdery component contains the starch derivative to be used according to the invention, and the liquid component contains an aqueous phase. Hair dyeing compositions or hair bleaching compositions generally have a high pH. Surprisingly, the starch derivative to be used according to the invention is stable also at the elevated pH of these products. The viscosity build up provided by the starch derivative to be used according to the invention enables the product to remain in place in the hair during use and enables the desired duration of exposure to be achieved. The starch to be used according to the invention can be easily dispersed in the aqueous medium without lumps. Polysaccharide thickening agents commonly used in hair treatment compositions, such as hydroxyethyl cellulose and xanthan gum, are typically difficult to disperse as

they form clumps and fish-eyes.

(50) For all the embodiments of the invention, as a function of the intended use, the composition according to the invention can contain additives selected from preservatives, perfumes, flavours, sun protection agents, antioxidants, vitamins, pharmaceutical active substances, fillers, sequestrants, colouring agents, bronzing agents, additional thickeners, inorganic salts, pH-regulators and/or pearlizing agents.

(51) The composition according to the invention has numerous advantages. The starch raw materials are derived from renewable sources, which is in accordance with the composition behaviour of a increasing number of consumers. Starch raw materials have long been used in foods and can be looked upon as unobjectionable. Compared with conventionally used carbomers they contain no toxic monomers and no solvents. They also contain no pesticides, which can, e.g., be present in plant gums.

(52) The invention will now be further illustrated by examples. The pH-values were measured electrometrically in the undiluted product. The viscosity values were measured with a Haake type RV 20-Rotovisko viscometer with the measuring devices mentioned in the examples, following a one minutes shear time in accordance with DIN 53019. The batches or mixtures were produced on a 1 kg scale with a paddle agitator. Homogenization took place with a Fema AG type S 100 SL 90 homogenizer at stage 8 and with a holding time of 100 ml/min.

(53) In the examples the following designations and trade names are used.

(1) Trade Name Manufacturer INCI Name Dehyquart A Henkel KGaA Cetrimonium Chloride Jaguar C-162 Rhone-Poulenc Hydroxypropyl Guar Hydroxypropyltrimonium Chloride Lanette 14 Henkel KGaA Myristyl Alcohol Tegopearl N 100 TH. Goldschmidt AG Glycol Distearate, Steareth-4 Texapon N 70 Henkel KGaA Sodium Laureth Sulfate Plantaren 1200 Henkel KGaA Lauryl Glucoside Tego Betain F TH. Goldschmidt AG Cocamidopropyl Betaine Elfan NS 242 A Akzo Nobel Sodium Laureth Sulfate Tego Betaine F 50 TH. Goldschmidt AG Cocamidopropyl Betaine Axol C62 TH. Goldschmidt AG Glyceryl Stearate Citrate Nipagin Nipa Labororien GmbH Methylparaben Nipazol Nipa Labororien GmbH Propylparaben Prisorine 3700 Unichema International Polyglycerol-3 Diisostearate Tegin 90 TH. Goldschmidt AG Glyceryl Stearate Miglycol 812 Huls AG Caprylic/Capric Triglyceride Sucro-Ester WE15 Gattefosse GmbH Sucrose Palmitate Cetiol 868 Henkel KGaA Octyl Stearate Phenonip Nipa Labororien GmbH Phenoxyethanol, Methylparaben, Butyl- paraben, Ethylparaben, Propylparaben Parsol MCX Givaudan-Roure Octyl Methoxycinnamate Uvinul MS 40 BASF Benzophenone-4 Natrium-Hyaluronat ROVI GmbH Sodium Hyaluronate Vitamin A-Palmitat BASF AG Retinyl Palmitate Vitamin E Acetat BASF AG Tocopheryl Acetate Ronoxan A

Hoffman La Roche AG Ascorbylpalmitate, D,L- $\alpha$ -Tocopherol, Lecithin Tego Care 215 TH. Goldschmidt AG Ceteareth-15, Glyceryl Stearate Tego Care 450 TH. Goldschmidt AG Polyglyceryl-3 Methylglucose Distearate Protegin TH. Goldschmidt AG Mineral Oil, Petrolatum, Ozokerite, Glyceryl Oleate, Lanolin Alcohol Neo PCL W/O E 2/066255 Dragoco Gerberding & Co. Cetearyl Octanoate, Ceresin, Lanolin, Sorbitan AG Sesquioleate, Stearyl Heptanoate, Paraffinum liquidum, Trihydroxystearin, BHT Hydroviton Dragoco Gerberding & Co. Aqua, Sodium Lactate, Lactic Acid, Glycerin, AG Serine, Sorbitol, TEA Lactate, Triethanolamine, Urea, Sodium Chloride, Lauryl Diethylenediaminoglycerine, Allantoin: Lauryl Aminopropylglycerine, Alcohol Texapon ALS Henkel KgaA Ammonium Lauryl Sulfate Rewopol SBFA Witco Surfactants GmbH Disodium Laurethsulfosuccinate Euxyl K400 Schulke & Mayr Methylidibromo Glutaronitril, Phenoxyethanol Sident 12DS Degussa Silica Texapon K1296 Pulver Henkel KgaA Ammonium Lauryl Sulfate Rewopol SBFA Witco Surfactants GmbH Disodium Laurethsulfosuccinate Euxyl K400 Schulke & Mayr Methylidibromo Glutaronitril, Phenoxyethanol Sident 12DS Degussa Silica Texapon K1296 Pulver Henkel KgaA Sodium Lauryl Sulfate Saccharin Na Bayer AG Sodium Saccharin Cutina FS 45 Henkel KgaA Palmitic Acid, Stearic Acid Luviskol K30 BASF AG PVP Cyclodextrin Beta W7 Wacker GmbH Cyclodextrin Pionier 4656 Hansen & Rosenthal Mineral Oil Vaseline Hansen & Rosenthal Petrolatum Titandioxid Les Colorants Wackherr S.A.

#### DETAILED DESCRIPTION:

##### (1) EXAMPLES

##### (2) Examples 1 to 3

(3) These examples illustrate the preparation of a hair rinse using the following formulation:

|                                                                                       | Example 3 | Example 1 | Example 2 (control) | Raw Materials                                 | wt. % |
|---------------------------------------------------------------------------------------|-----------|-----------|---------------------|-----------------------------------------------|-------|
| Water                                                                                 | 87.050    | 87.050    | 89.750              | Dehyquart A                                   | 3.000 |
| Jaguar C-162                                                                          | 0.500     | 0.500     | 0.500               | Pregelatinized, hydroxypropylated             | 2.700 |
| di-starch phosphate of waxy maize starch in the form of loosely agglomerated granules | 2.700     | --        | --                  | Hydropropylated di-starch phosphate           | --    |
| of tapioca starch*                                                                    | 2.700     | --        | --                  | Lanette 14                                    | 3.000 |
|                                                                                       | 3.000     | 3.000     | 3.000               | Tegoppearl N                                  | 100   |
|                                                                                       | 3.000     | 3.000     | 3.000               | Perfume                                       | 0.400 |
|                                                                                       | 0.400     | 0.400     | 0.400               | Citric Acid                                   | 0.050 |
|                                                                                       | 0.050     | 0.050     | 0.050               | Benzoic Acid                                  | 0.300 |
|                                                                                       | 0.300     | 0.300     | 0.300               | Specification values for:                     |       |
| pH                                                                                    | 5.1       | 5.2       | 5.1                 | Viscosity MV stage 1 (mpas)                   | 5100  |
|                                                                                       |           |           |                     |                                               | 1350  |
|                                                                                       |           |           |                     |                                               | 1100  |
|                                                                                       |           |           |                     | *Farinex VA 70T (Avebe/Stadex, Malmo, Sweden) |       |

(4) Into the water heated to about 55.degree. C. were stirred Dehyquart A, benzoic acid and the starch derivatives (except for Example 3 which contained no starch). When this mixture was homogenized, Jaguar C-162 and citric acid were stirred in. Lanette 14 which contained no starch was heated to 55.degree. C. and stirred into the mixture. After cooling to about 40.degree. C., accompanied

by stirring, Tegoparl N 100 and the perfume were added to the mixture. After cooling to about 25.degree. C., accompanied by stirring, a medium-viscosity, pearly bright dispersion was obtained in Example 1. Examples 2 and 3 were too watery and could not be used.

(5) In use tests on normal damaged hair, the hair rinse according to Example 1 was given a good evaluation. Poor results were obtained with Examples 2 and 3 with regards to their dispersibility on wet hair and wet combability.

(6) The storage tests for Example 1 at -18.degree. C., +4.degree. C., ambient temperature (18 to 25.degree. C.), +30.degree. C. and +40.degree. C. after one month revealed a product substantially unchanged compared with the specifications. Phase separation occurred after one day with Examples 2 and 3.

(7) Examples 4 to 6

(8) These examples illustrate the preparation of a shampoo, using the following formulation:

| (2)                                                                                      | Example 6 | Example 4 | Example 5 (control) | Raw material                                 | wt. % | wt. %       |
|------------------------------------------------------------------------------------------|-----------|-----------|---------------------|----------------------------------------------|-------|-------------|
| % Water                                                                                  | 73.21     | 73.21     | 73.81               | Texapon N 70                                 | 11.00 | 11.00 11.00 |
| Plantaren 1200                                                                           | 3.50      | 3.50      | 3.50                | Sodium benzoate                              | 0.40  | 0.40 0.40   |
| Citric acid                                                                              | 0.49      | 0.49      | 0.49                | Potassium Sorbate                            | 0.20  | 0.20 0.20   |
| Tego Betaine F                                                                           | 4.20      | 4.20      | 4.20                | Sodium chloride, 22% solution in             | 6.00  | 6.00 6.00   |
| D-Panthenol                                                                              | 0.10      | 0.10      | 0.10                | Pregelatinized, hydroxypropylated            | 0.60  | --          |
| -- di-starch phosphate of waxy maize starch in the form of loosely agglomerated granules |           |           |                     | Hydroxypropylated di-starch                  | --    | 0.60 --     |
| phosphate of potato starch*                                                              |           |           |                     | Perfume                                      | 0.30  | 0.30 0.30   |
| Specification values for: pH                                                             | 5.0       | 5.1       | 5.2                 | Viscosity NV stage 1 (mpas)                  | 11100 | 7200        |
|                                                                                          | 7000      |           |                     | *Farinex VA 70 (Avebe/Stadex, Malmo, Sweden) |       |             |

(9) Into the water at about 25.degree. C. were successively stirred Plantaren 1200, sodium benzoate, potassium sorbate, citric acid, Tego Betaine F, D-Panthenol and the starch derivatives (except for Example 6 which contained no starch). When the mixture became homogeneous, the 22% sodium chloride solution was stirred in. Accompanied by vigorous stirring Texapon N 70 was added. The perfume was stirred in when the mixture became homogenous.

(10) According to Example 4 a slightly opalescent, viscous shampoo was obtained. Example 5 and 6 had a much too low viscosity.

(11) When used on hair, the shampoo according to Example 4 had good wet combability characteristics, besides a fine-bubble foam. Examples 5 and 6 formed a much larger bubble foam than Example 4 on the hair and the wet comability was inferior.

(12) The storage tests for the product according to Example 4 at -18.degree. C., +4.degree. C., ambient temperature (18 to 25.degree. C.) and +30.degree. C. after one month revealed a product largely unchanged compared with the specifications. Example 5 showed phase separation after two days at ambient temperature.

(13) The viscosity of Example 4 was in fact higher than the indicated value because the measuring range of the viscosimeter used was exceeded.

(14) Example 7 to 9

(15) These examples illustrate the preparation of foam bath using the following formulation:

|                                                                                          | Example 9 | Example 7 | Example 8 (control) | Raw material                                 | wt. %         | wt. %  |
|------------------------------------------------------------------------------------------|-----------|-----------|---------------------|----------------------------------------------|---------------|--------|
| Elfan NS 242 A                                                                           | 89.38     | 89.38     | 90.08               | Glycerin (87%)                               | 2.72          | 2.72   |
| Tego betaine F50                                                                         | 3.00      | 3.00      | 3.00                | Plantaren 1200                               | 2.00          | 2.00   |
| Potassium sorbate                                                                        | 0.20      | 0.20      | 0.20                | Sodium benzoate                              | 0.40          | 0.40   |
| Citric acid                                                                              | 0.80      | 0.80      | 0.80                | Pregelatinized, hydroxypropylated            | 0.70          | --     |
| -- di-starch phosphate of waxy maize starch in the form of loosely agglomerated granules |           |           |                     | Hydroxypropylated di-starch                  | --            | 0.70   |
| -- phosphate of potato starch*                                                           |           |           |                     | Perfume                                      | 0.80          | 0.80   |
| Specification values for: pH                                                             | 5.0       | 5.1       | 4.9                 | Viscosity MV stage 1                         | 20.degree. C. | (mpas) |
|                                                                                          | 14500     | 7500      | 7200                | *Farinex VA 70 (Avebe/Stadex, Malmo, Sweden) |               |        |

(16) Into the Elfan NS 242 A at about 25.degree. C. were successively stirred Plantaren 1200, sodium benzoate, potassium sorbate, citric acid, Tego betaine F 50 and its starch derivatives (except for Example 9 which contained no starch derivative). The perfume was added, accompanied by stirring, when the mixture became homogeneous.

(17) Example 7 gave a slightly opalescent, viscous foam bath with pleasant use characteristics. In bath water foams both of Examples 8 and 9 give a larger-bubble foam than Example 7. In addition, the bath foam of Example 8 gave a negative, sandy skin feel.

(18) The storage tests for the product of Example 7 at -18.degree. C., +40.degree. C., ambient temperature (18 to 25.degree. C.) and +30.degree. C. after one month revealed a product largely unchanged compared with the specifications.

(19) After storing for two days at ambient temperature, phase separation occurred with the product of Example 8.

(20) Examples 10 to 15

(21) These examples illustrate the preparation of an O/W body

lotion using the following formulation:

(4) Example Exam- Exam- Exam- 13 ple 10 ple 11 ple 12 (control)  
 Raw material wt. % wt. % wt. % wt. % Water 76.54 76.54 76.54 79.54  
 Axol C62 3.00 3.00 3.00 3.00 D-Panthenol 0.25 0.25 0.25 0.25 87%  
 glycerin 3.00 3.00 3.00 3.00 Pregelatinized, hydroxy- 3.00 -- -- --  
 propylated acetylated di-starch phosphate of waxy maize starch in the  
 form of loosely agglomerated granules Pregelatinized, waxy maize --  
 3.00 -- -- starch acetate, crosslinked with adipic acid-acetic acid  
 anhydride in the form of loose, agglomerated granules Pregelatinized,  
 hydroxy- -- -- 3.00 -- propylated di-starch phosphate of tapioca  
 starch, granular Nipagin 0.50 0.50 0.50 0.50 Nipasol 0.15 0.15 0.15  
 0.15 Refined soy oil 4.00 4.00 4.00 4.00 Refined coconut oil 8.00  
 8.00 8.00 8.00 Prisorine 3700 0.70 0.70 0.70 0.70 Vitamin E acetate  
 0.01 0.01 0.01 0.01 Jojoba oil 0.50 0.50 0.50 0.50 Perfume 0.35 0.35  
 0.35 0.35 Specification value for: pH 5.3 5.2 5.2 5.3 Viscosity MV  
 after 1 day (mpas) 1250 1150 660 150 Example Example 14 15 Raw  
 material wt. % wt. % Water 76.54 76.74 Axol C62 3.00 3.00 D-Panthenol  
 0.25 0.25 Glycerin (87%) 3.00 3.00 Pregelatinized, hydroxypropylated  
 di-starch 3.00 3.00 phosphate of waxy maize starch in the form of  
 loosely agglomerated granules Nipagin 0.50 0.50 Nipasol 0.15 0.15  
 Miglycol 812 4.00 4.00 Paraffin oil 8.00 8.00 Prisorine 3700 0.70  
 Tegin 90 0.50 Vitamin E acetate 0.01 0.01 Jojoba oil 0.50 Cetiol 868  
 0.50 Perfume 0.35 0.35 Specification values for: pH 5.1 5.5 Viscosity  
 MV after 1 day (mpas) 1250 2500

(22) Axol C62, the starch derivatives (except for Example 13 which contained not starch derivative), Nipagin, Nipasol were heated, accompanied by stirring, at 75.degree. C. in 2/3 of the total water quantity until the mixture was homogeneous, followed by the addition of D-Panthenol and 87% glycerin to the mixture. The coconut oil, soy oil, Prisorine 3700 or Tegin 90 and vitamin E acetate were heated to about 60.degree. C. and added to the water phase, accompanied by stirring. When this mixture was homogeneous, the remaining quantity of the water at about 20.degree. C. was added to the mixture, accompanied by stirring. The perfume was added, accompanied by stirring, at about 40.degree. C. The mixture was then homogenized with a homogenizer and stirred on to about 25.degree. C.

(23) When used on the skin, the emulsions according to Examples 10, 11, 12, 14 and 15 had an excellent skin feel. The emulsion according to Example 13 was evaluated as having no content.

(24) The storage tests for Examples 10, 11, 12, 14 and 15 at -18.degree. C., +4.degree. C., ambient temperature (18 to 25.degree. C.), +30.degree. C. and +40.degree. C revealed that after 3 months storage of the product were largely unchanged compared with the specifications. After prolonged storage, the lotion according to Example 11 had a slightly acid odor.

(25) At all the storage temperatures the emulsion according to Example 13 separated after at the latest two days.

(26) Examples 16 to 18

(27) These examples illustrate the preparation of an O/W cosmetic cream using the following formulation:

(5) Example Example Example 18 16 17 (control) Raw material wt. %  
 wt. % wt. % Water 55.735 55.735 60.735 Nipagin 0.350 0.350 0.350  
 Nipasol 0.150 0.150 0.150 D-Panthenol 0.200 0.200 0.200 Vitamin E  
 acetate 0.500 0.500 0.500 Glycerin (87%) 5.000 5.000 5.000 Sucro-  
 ester WE 15 2.000 2.000 2.000 Axol C 62 2.000 2.000 2.000 Prisorine  
 3700 0.700 0.700 0.700 Perfume 0.100 0.100 0.100 Refined coconut fat  
 18.000 18.000 18.000 Pregelatinized, hydroxypropylated 5.000 -- --  
 di-starch phosphate of waxy maize starch in the form of loosely  
 agglomerated granules Hydroxypropylated di-starch -- 5.000 --  
 phosphate of tapioca starch\* Refined soy oil 8.000 8.000 8.000 Sodium  
 hyaluronate 0.005 0.005 0.005 Vitamin A-palmitate 0.060 0.060 0.060  
 Ronoxan A 0.200 0.200 0.200 Jojoba oil 2.000 2.000 2.000  
 Specification values for: pH 5.1 5.5 5.3 Viscosity SV stage 4  
 (20.degree. C.) 6640 too low too low viscosity, viscosity, not meas-  
 not meas- urable urable \*Farinex VA 70T (Avebe/Stadex, Malmo, Sweden)

(28) The starch derivatives (except for Example 18 where not starch derivative was present) were stirred in water for about 10 minutes at 80.degree. C., followed by the addition to the mixture, accompanied by stirring, of Sucro-ester WE 15 and Axol C62, and then D-Panthenol, Nipagin, Nipasol and glycerin. The coconut oil, soy oil, Prisorine 3700 and vitamin E acetate were separately heated to about 60.degree. C. and added to the water phase, accompanied by stirring. Accompanied by stirring, the mixture is cooled to about 40.degree. C. and sodium hyaluronate, vitamin A-palmitate, Ronoxan A, jojoba oil and perfume were added, accompanied by stirring. The mixture was then homogenized with a homogenizer and stirred on to about 25.degree. C.

(29) The cream according to Example 16 has excellent cosmetic properties when used on the skin. The evaluation of the cream of Example 17 was much inferior. The product of Example 18 become inhomogeneous shortly after application to the skin.

(30) The storage tests of the cream according to Example 16 at -18.degree. C., +4.degree. C., ambient temperature (18 to 25.degree. C.), +30.degree. C. and +40.degree. C. revealed a substantially unchanged product after 3 months. Examples 17 and 18, after 3 days under all test conditions, revealed inhomogeneities.

(31) Examples 19 to 21



(32) These examples illustrate the preparation of an alcohol-containing lotion with a deodorant action using the following formulation:

(6) Example Example Example 21 19 20 (control) Raw material wt. %  
wt. % wt. % Water 60.24 60.24 62.24 Axol C62 3.00 3.00 3.00  
Pregelatinized, hydroxypropylated 2.00 -- -- di-starch phosphate of  
waxy maize starch in the form of loosely agglomerated granules  
Hydroxypropylated di-starch -- 2.00 -- phosphate of tapioca starch\*  
D-Panthenol 0.40 0.40 0.400 Triethyl citrate 1.00 1.00 1.00 Farnesol  
0.50 0.50 0.50 Prisorine 3700 0.56 0.56 0.56 Glycerin (87%) 3.00 3.00  
3.00 Perfume 0.80 0.80 0.80 Refined soy oil 8.50 8.50 8.50  
Specification values for: pH 5.5 5.2 5.4 Viscosity SV stage 4 (mpas)  
700 150 120 \*Farinex VA 70 (Avebe/Stadex, Malmo, Sweden)

(33) The starch derivatives (except for Example 21 where no starch derivative was used) were strewn in water at 80.degree. C., stirred for about 10 min and then Axol C62 was added to the mixture, accompanied by stirring, followed by D-Panthanol and glycerin. The soy oil and Prisorine 3700 were separately heated to about 60.degree. C. and added to the aqueous phase, accompanied by stirring. Accompanied by stirring cooling took place to about 40.degree. C. and ethanol, triethyl citrate, Farnesol and perfume were added, accompanied by stirring. The mixture was then homogenized with a homogenizer and stirred on to about 25.degree. C.

(34) When used on the skin, a positive evaluation with regards to its use characteristics was given to the lotion of Example 19. Examples 20 and 21 were considered to have less content or be watery. Example 20 was also considered to be sandy.

(35) The storage tests on Example 19 at -18.degree. C., +4.degree. C., ambient temperature (18 to 25.degree. C.), +30.degree. C. and +40.degree. C. revealed a substantially unchanged product after 3 months.

(36) However, the products of Examples 20 and 21 revealed phase separation at ambient temperature after 1 day.

(37) Examples 22 to 24

(38) These examples illustrate the preparation of an alcohol-containing cream with light protection action.

(7) Example Example Example 24 22 23 (control) Raw material wt. %  
wt. % wt. % Water 47.40 47.40 49.80 Axol C62 3.20 3.20 3.20 Uvinul MS  
40 2.00 2.00 2.00 Parsol MCX 3.00 3.00 3.00 Pregelatinized,  
hydroxypropylated 2.40 -- -- di-starch phosphate of waxy maize starch  
in the form of loosely agglomerated granules Hydroxypropylated di-

starch -- 2.40 -- phosphate of potato starch\* D-Panthenol 0.40 0.40  
 0.40 Prisorine 3700 0.56 0.56 0.56 Avocado oil 0.80 0.80 0.8 Jojoba  
 oil 0.80 0.80 0.80 Glycerin (87%) 3.20 3.20 3.20 Perfume 3.20 3.20  
 3.20 94.5 wt. % ethanol 20.00 20.00 20.00 Refined coconut oil 16.00  
 16.00 16.00 Specification values for: pH 5.4 5.3 5.4 Viscosity M  
 stage 4 (mpas) 3200 1100 800 \*Farinex VA 70 (Avebe/Stadex, Malmo,  
 Sweden)

(39) The starch derivatives (except for in Example 24 where no starch derivative was used) were strewn into the water at 80.degree. C., stirred for about 10 min., followed by the addition to the mixture of Axol C62, accompanied by stirring and then followed by Uvinul MS 40, D-Panthenol and glycerin. The coconut oil, avocado oil, jojoba oil, Parsol MCX and Prisorine 3700 were separately heated to about 60.degree. C. and added to the aqueous phase, accompanied by stirring. Accompanied by stirring, cooling took place to about 40.degree. C. and ethanol and perfume were added, accompanied by stirring. The mixture was homogenized with a homogenizer and stirred on to about 25.degree. C.

(40) The use characteristics of the product of Example 22 were assessed as good.

(41) The storage tests at -18.degree. C., +4.degree. C., ambient temperature (18 to 25.degree. C.), +30.degree. C. and +40.degree. C. revealed a largely unchanged product after 3 months.

(42) The use characteristics of the products according to Examples 23 and 24 were considered to be less satisfactory. Example 23 also gave a sandy impression.

(43) The products of Examples 23 and 24 suffered phase separation after 1 day.

(44) Examples 25 to 34

(45) These examples illustrate the preparation of an O/W body lotion using the following formulation:

| (8)                                                                | Exam- | Exam- | Exam- | Exam- | ple 25                                  | ple 26 | ple 27 | ple 28 | Raw   |
|--------------------------------------------------------------------|-------|-------|-------|-------|-----------------------------------------|--------|--------|--------|-------|
| material                                                           | wt. % | wt. % | wt. % | wt. % | Water                                   | 76.54  | 76.54  | 76.54  | 79.54 |
| Axol C62                                                           | 3.00  | 3.00  | 3.00  | 3.00  | D-Panthenol                             | 0.25   | 0.25   | 0.25   | 0.25  |
| Glycerin (87%)                                                     | 3.00  | 3.00  | 3.00  | 3.00  | Maize starch, modified with             | 3.00   | --     | --     | --    |
| octenyl succinanhydride, acid-treated Pregelatinized maize starch, | --    | --    | --    | --    | drum dried Pregelatinized maize starch, | --     | --     | 3.00   | --    |
| granular Pregelatinized waxy maize starch                          | --    | --    | --    | --    | Nipagin                                 | 0.50   |        |        |       |
|                                                                    | 0.50  | 0.50  | 0.50  | 0.50  | Nipasol                                 | 0.15   | 0.15   | 0.15   | 0.15  |
| Refined soy oil                                                    | 4.00  | 4.00  | 4.00  | 4.00  | Refined coconut oil                     | 8.00   | 8.00   | 8.00   | 8.00  |
| Prisorine 3700                                                     | 0.70  | 0.70  | 0.70  | 0.70  | Vitamin E acetate                       | 0.01   | 0.01   | 0.01   | 0.01  |
| Jojoba oil                                                         | 0.50  |       |       |       |                                         |        |        |        |       |

0.50 0.50 0.50 Perfume 0.35 0.35 0.35 0.35 Specification values for:  
 pH 5.6 5.5 5.7 5.6 Viscosity MV (mpas) 125 180 200 250 Exam- Exam-  
 Exam- Exam- ple 29 ple 30 ple 31 ple 32 Raw material wt. % wt. % wt.  
 % wt. % Water 76.54 76.54 76.54 79.54 Axol C62 3.00 3.00 3.00 3.00 D-  
 Panthenol 0.25 0.25 0.25 0.25 Glycerin (87%) 3.00 3.00 3.00 3.00  
 Thin-boiling, hydroxypropylated 3.00 -- -- -- maize starch  
 Hydroxypropylated di-starch -- 3.00 -- -- phosphate of waxy maize  
 starch Hydroxypropylated di-starch -- -- 3.00 -- phosphate  
 Hydroxypropylated di-starch -- -- -- 3.00 phosphate of maize starch  
 Nipagin 0.50 0.50 0.50 0.50 Nipasol 0.15 0.15 0.15 0.15 Refined soy  
 oil 4.00 4.00 4.00 4.00 Refined coconut oil 8.00 8.00 8.00 8.00  
 Prisorine 3700 0.70 0.70 0.70 0.70 Vitamin E acetate 0.01 0.01 0.01 0.01  
 0.01 Jojoba oil 0.50 0.50 0.50 0.50 Perfume 0.35 0.35 0.35 0.35  
 Specification values for: pH 5.1 5.2 5.4 5.0 Viscosity MV stage 4  
 (mpas) 1010 Example Example 33 34 Raw material wt. % wt. % Water  
 76.54 76.74 Axol C62 3.00 3.00 D-Panthenol 0.25 0.25 Glycerin (87%)  
 3.00 3.00 Hydroxypropylated di-starch phosphate of potato 3.00 --  
 starch\* Hydroxypropylated di-starch phosphate of -- 3.00 tapioca  
 starch\*\* Nipagin 0.50 0.50 Nipasol 0.15 0.15 Refined soy oil 4.00  
 4.00 Refined coconut oil 8.00 8.00 Prisorine 3700 0.70 0.70 Vitamin E  
 acetate 0.01 0.01 Jojoba oil 0.50 0.50 Perfume 0.35 0.35  
 Specification values for: pH 5.6 5.6 Viscosity KV (mpas) 60 50  
 \*Farinex VA 70 (Avebe/Stadex, Malmo, Sweden) \*\*Farinex VA 70T  
 (Avebe/Stadex, Malmo, Sweden)

(46) Preparation took place as in Examples 10 to 15.

(47) The storage stability was inadequate in Examples 25 to 32 and there was a clear phase separation after a short time. The mixtures of Examples 33 and 34 had a very limited, unusable viscosity for this product type. After 2 days a phase separation was detected at ambient temperature. A sandy skin feel was noted in use tests.

(48) Examples 35 and 36

(49) These examples illustrate the preparation of an O/W body cream, using the following formulation:

(9) Example Example 35 36 Raw material wt. % wt. % Water 65.76  
 66.36 Tego Care 215 3.00 -- Tego Care 450 -- 3.00 Tegin 90 0.60 -- D-  
 Panthenol 0.13 0.13 Glycerin (87%) 3.00 3.00 Pregelatinized,  
 hydroxypropylated di-starch 5.00 5.00 phosphate of waxy maize starch  
 in the form of loosely agglomerated granules Phenonip 0.90 0.90  
 Vitamin A-palmitate 0.06 0.06 Refined soy oil 10.00 10.00 Refined  
 coconut oil 10.00 10.00 Prisorine 3700 0.70 0.70 Vitamin E acetate  
 0.50 0.50 Perfume 0.35 0.35 Specification values for: pH 7.0 7.2  
 Viscosity MV (mpas) 3800 4400

(50) Pregelatinized, hydroxypropylated di-starch phosphate of waxy maize starch in the form of loose-agglomerated grains are heated,

accompanied by stirring, at 80.degree. C. in the water until the mixture is homogeneous, followed by the addition to the mixture of Phenonip, D-Panthenol and 87% glycerin and then the emulsifiers Tego Care 215 or Tego Care 450 were stirred in. The coconut oil, soy oil, Prisorine 3700, Tegin 90 and vitamin E acetate were heated to about 60.degree. C. and added to the aqueous phase, accompanied by stirring. When the mixture was homogeneous, it was cooled, accompanied by stirring. At about 40.degree. C. the perfume and vitamin A-palmitate are added, accompanied by stirring. The mixture was then homogenized with a homogenizer and stirred on to about 25.degree. C.

(51) The use characteristics of the product according to Examples 35 and 36 were considered to be good.

(52) The storage tests at -18.degree. C., +4.degree. C., ambient temperature (18 to 25.degree. C.), +30.degree. C. and +40.degree. C. revealed a largely unchanged product after 3 months.

(53) Examples 37 to 39

(54) These examples illustrate the preparation of a shaving foam using the following formulation:

|                                   | Example 37 | Example 38 | Example 39 | Raw material                                                                          | wt. %   | wt. % | wt. % |
|-----------------------------------|------------|------------|------------|---------------------------------------------------------------------------------------|---------|-------|-------|
| % Water                           | 73.922     | 73.922     | 74.422     | Propane/butane                                                                        | 3.5 bar | 5.000 | 5.000 |
| Eumulgin B2                       | 1.000      | 1.000      | 1.000      | Glycerin (87%)                                                                        | 8.730   | 8.730 | 8.730 |
| Pregelatinized, hydroxypropylated | 0.500      | --         | --         | di-starch phosphate of waxy maize starch in the form of loosely agglomerated granules |         |       |       |
| Hydroxypropylated di-starch       | --         | 0.500      | --         | phosphate of tapioca starch*                                                          |         |       |       |
| Cutina FS 45                      | 5.277      | 5.277      | 5.277      | Myristic acid                                                                         | 1.251   | 1.251 | 1.251 |
| Triethanol amine (min. 99%)       | 3.030      | 3.030      | 3.030      | Luviskol K30                                                                          | 0.490   |       |       |
|                                   | 0.490      | 0.490      |            | Perfum                                                                                | 0.800   | 0.800 | 0.800 |
|                                   | 8.5        | 8.5        |            | Specification values for: pH                                                          | 8.5     |       |       |
|                                   |            |            |            | Viscosity MV (mpas)                                                                   | 1200    | 430   | 360   |
|                                   |            |            |            | *Farinex VA 70T                                                                       |         |       |       |

(Avebe/Stadex, Malmo, Sweden)

(55) The starch derivative (except for in Example 39 where no starch derivative was used) was heated in the water at 75.degree. C., accompanied by stirring, until the mixture was homogeneous, followed by the addition to the mixture of Cutina FS 45, myristic acid, Eumulgin B2 and 87% glycerin. After the fat components had melted, triethanol amine was added to the mixture, accompanied by stirring. After cooling to about 40.degree. C., the perfume and Luviskol K30 were added, accompanied by stirring. The mixture was then homogenized with a homogenizer and stirred on to about 25.degree. C. This active substance solution was filled into an aerosol can, the valve was fitted and the can was filled under pressure with the propellant propane/butane, after which the spray head was fitted to the can.

(56) The use characteristics of the product according to Example 37 were evaluated as good. The products of Examples 38 and 39 were subject to a much poorer evaluation.

(57) The storage tests the of product of Example 37 at -18.degree. C., +4.degree. C., ambient temperature (18 to 25.degree. C.), +30.degree. C. and +40.degree. C. revealed a largely unchanged product after 3 months. The storage tests for the products of Examples 38 and 39 revealed phase separation under the same conditions after 7 days.

(58) Examples 40 to 42

(59) These examples illustrate the preparation of a W/O body cream using the following formulation:

(11) Example Example Example 42 40 41 (control) Raw material wt. %  
 wt. % wt. % Water 55.93 55.93 56.68 Protegin 20.00 20.00 20.00 Epsom  
 Salt 0.30 0.30 0.30 Glycerin (87%) 2.00 2.00 2.00 Pregelatinized,  
 hydroxypropylated 0.75 -- -- di-starch phosphate of waxy maize starch  
 in the form of loosely agglomerated granules Hydroxypropylated di-  
 starch -- 0.75 -- phosphate of tapioca starch\* Nipagin 0.15 0.15 0.15  
 Nipasol 0.05 0.05 0.05 Vitamin E acetate 0.10 0.10 0.10 Redefined  
 coconut oil 13.00 13.00 13.00 Neo PCL W/O 5.00 5.00 5.00 Butyl  
 hydroxytoluene 0.02 0.02 0.02 Hydroviton moisturizing factor 2.00  
 0.50 0.50 Perfume 0.70 0.70 0.70 Specification values for: pH (1) (1)  
 (1) Viscosity SV stage 4 (mpas) 21400 14300 15000 (1)-not measurable,  
 because W/O system present \*Farinex VA 70T (Avebe/Stadex, Malmo,  
 Sweden)

(60) The starch derivative (except for in Example 42 where no starch derivative was used), Nipagin, Nipasol and Epsom salts were heated, accompanied by stirring, in the water quantity at 80.degree. C. until the mixture was homogeneous, followed by the addition to the mixture of 87% glycerin. The coconut oil, Protegin, Neo PCL W/O and butyl hydroxytoluene were heated to about 75.degree. C. and added to the aqueous phase, accompanied by stirring. When the mixture was homogeneous, it was cooled, accompanied by stirring. At about 40.degree. C. the perfume, hydroviton moisturizing factor and vitamin E acetate were added, accompanied by stirring. The mixture was then homogenized with a homogenizer and stirred on to about 25.degree. C. The use characteristics of the product of Example 40 were evaluated as good.

(61) The storage tests at -18.degree. C., +4.degree. C., ambient temperature (18 to 25.degree. C.), +30.degree. C. and +40.degree. C. revealed a largely unchanged product after 5 months.

(62) The phase stability for the products of Examples 41 and 42 was

not adequate.

(63) Examples 43 to 45

(64) These examples illustrate the preparation of a dishwashing composition using the following formulation:

(12) Example Example Example 45 43 44 (control) Raw material wt. %  
wt. % wt. % Water 20.90 20.90 23.90 Texapon ALS 50.00 50.00 50.00  
Plantaren 1200 5.00 5.00 5.00 Rewopol SBFA 15.00 15.00 15.00 Ethanol  
5.00 5.00 5.00 Citric acid 0.50 0.50 0.50 Euxyl K400 0.20 0.20 0.20  
D-Panthenol 0.10 0.10 0.10 Pregelatinized, hydroxypropylated, 3.00 --  
-- acetylated di-starch phosphate of waxy maize starch in the form of  
loosely agglomerated granules Hydroxypropylated di-starch -- 3.00 --  
phosphate of tapioca starch\* Perfume 0.30 0.30 0.30 Specification  
values for: pH 5.5 5.4 5.7 Viscosity MV (mpas) 4200 1400 1200  
\*Farinex VA 70T (Avebe/Stadex, Malmo, Sweden)

(65) Into the water at about 25.degree. C. were successively stirred Texapon ALS, Plantaren 1200, Rewopol SBFA, Euxyl K400, citric acid and the starch derivatives (except for Example 45 where no starch was present). D-Panthenol, ethanol and perfume were stirred in when the mixture became homogeneous.

(66) According to Example 43 a slightly opalescent, viscous dishwashing composition was obtained. The compositions of Examples 44 and 45 had a much lower viscosity.

(67) In use, apart from a stable foam, the dishwashing composition had a good cleaning action and a good skin feel. The compositions of Examples 44 and 45 form a much larger-bubble foam than the composition of Example 43.

(68) The storage tests of the product according to Example 43 at -18.degree. C., +40.degree. C., ambient temperature (18 to 25.degree. C.) and +30.degree. C. gave a largely unchanged product compared with the specifications after 1 month.

(69) The composition of Example 44 revealed a phase separation at ambient temperature after 2 days.

(70) Example 46

(71) This example illustrates the preparation of a dental cream using the following formulation:

(13) Raw material Example 46 wt. % Water 24.70 Sodium hydrogen carbonate 20.00 Sident 12DS 15.00 Glycerin 15.00 Sorbitol (70%) 10.00 Sodium pyrophosphate 4.00 Sodium carbonate 2.00 Texapon K1296 powder

2.00 Pregelatinized, hydroxypropylated di-starch 5.00 phosphate of waxy maize starch in the form of loosely agglomerated granules Sodium saccharine 0.10 Sodium fluoride 0.20 Titanium dioxide 1.00 Flavor 1.00 Specification values for: pH 9.0 Viscosity MV (mpas) 14500

(72) Into the water at about 25.degree. C. were successively stirred sodium hydrogen carbonate, sodium carbonate, sodium fluoride, the starch derivative, Sident 12DS, glycerin, 70% sorbitol, sodium pyrophosphate, Texapon K1296, sodium saccharine, titanium dioxide and flavor. Homogenization took place until the mixture is homogeneous.

(73) According to Example 46, a white, high viscosity dental cream were obtained.

(74) In use the dental cream gives a good cleaning action and a pleasant mouth feel, apart from a dense, stable foam.

(75) The storage tests for the product according to Example 46 at -18.degree. C., +4.degree. C., ambient temperature (18 to 25.degree. C) and +30.degree. C. gave a largely unchanged product compared with the specifications after 1 month.

(76) Example 47

(77) This example illustrates the preparation of an emulsifier-free O/W body lotion using the following formulation:

(14) Raw material Example 47 wt. % Water 77.700 Cyclodextrin beta W7 1.000 Glycerin (87%) 5.000 Pregelatinized, hydroxypropylated di-starch 5.000 phosphate of waxy maize starch in the form of loosely agglomerated granules Nipagin 0.400 Nipasol 0.100 Pioneer 4656 5.000 Vaseline 5.000 Titanium dioxide 0.500 Perfume 0.300 Specification values for: pH 6.3 Viscosity MV after 1 day (mpas) 2250

(78) The cyclodextrin, starch derivative, Nipagin, Nipasol and titanium dioxide were heated, accompanied by stirring, at 75.degree. C. in 2/3 of the water until the mixture was homogeneous, followed by the glycerin addition. Pioneer 4656 and Vaseline were heated to about 60.degree. C. and added to the water phase. The remaining water quantity was then added. The perfume was added at 40.degree. C. and the mixture was homogenized with a homogenizer. In use the body lotion had an excellent skin feel and was stable for at least six months.

(79) Example 48

(80) This example illustrates the preparation of a thickened hair bleaching system using the following formulations:

(15) Raw material g Component A Ammonium persulfate 1,50 Potassium hydrogen tartrate 1,50 Sodium carbonate 1,50 Sodium lauryl sulphate (Stepanol WA-100) 0,50 Hydroxypropylated distarch phosphate of 0,75 waxy maize starch, pregelatinized according to US 4 280 851 Magnesium hydroxide 22,13 Aluminum hydroxide 22,12 Component B Hydrogen peroxide 50% 12,00 Distilled water 88,00

(81) The ingredients of A were dry blended. The ingredients of B were mixed. For use, the two components were combined and applied to the hair. After combining, the hair bleaching composition had a viscosity of 30.219 mPas (Brookfield Heliopath, 10 rpm). For comparison, the identical formulation was prepared without the starch derivative. The composition had a viscosity of 431 mPas after blending.

(82) Example 49

(83) This example investigates the behaviour of different starch thickening agents in different environments. Each starch was added as a 10% solid dispersion to yield a 5% by weight final concentration in the following aqueous systems:

(84) Condition:

(85) 1) Water

(86) 2) 2% NH<sub>4</sub> OH

(87) 3) 2% NH<sub>4</sub> OH and 1% polymeric conditioning agent (Polyquaternium 6)

(88) 4) 2% NH<sub>4</sub> OH and 1% monomeric conditioning agent (Cetrimonium chloride).

(89) The 10% dispersions of the uncooked starches were prepared by boiling for 30 minutes while stirring. The 10% dispersions of the pre-gelatinized starches were prepared by mixing the starch into water at ambient temperature. The initial viscosities of the starch formulations and the viscosity development over time were recorded.

(16) Starch Condition Viscosity mPas, 45.degree. C. Spray-dried pregelatinized 1 7400 quaternized cross-linked waxy 2 2680 maize starch 3 3040 4 2420 Hydroxypropylated distarch 1 7892 phosphate waxy maize starch, 2 14092 uncooked high degree of 3 18092 substitution 4 7832 Drum dried pre-gelatinized 1 3100 hydroxypropylated distarch 2 5260 phosphate waxy maize starch, 3 7940 moderate degree of substitution 4 1532 Spray-dried pre-gelatinized 1 3452 hydroxypropylated distarch 2 12840 phosphate, waxy maize starch, 3 14132 moderate degree of 4 2740 substitution Multicarboxylated potato



starch, 1 27472 uncooked 2 25500 3 3732 4 0 Hydroxypropylated waxy  
maize 1 600 starch, uncooked 2 1000 3 2800 4 1952 None 1 0 2 0 3 0 4  
0

(90) Excluding the multi-carboxylated starch, the most efficient thickening agents were the hydroxypropyl distarch phosphates. The carboxylated starch was more efficient only in the absence of cationic compounds. Cationic compounds, however, are incompatible with this starch as precipitation was observed with the monomeric conditioning agent after one day and was observed with the polymeric conditioning agents after two days. All other starches showed good compatibility with the cationic compounds. Further, the pre-gelatinization process influences the performance characteristics of the starch derivatives. Thus, the drum-dried hydroxypropylated distarch phosphate is much more efficient than the comparable non-crosslinked hydroxypropyl starch. Therefore, a particular derivatization is required for optimum efficiency. Surprisingly, the hydroxypropyl distarch phosphate thickener efficiency was enhanced by the effect of the base. This makes the hydroxypropylated distarch phosphates particularly interesting for application in hair treatment products such as hair dyeing compositions and hair bleaching compositions. The viscosities of the pre-gelatinized starches and the cooking starches cannot directly be compared because the extent of starch swelling and shear degradation will be different.

(91) In a further experiment, the influence of the pre-gelatinization process, of agglomeration, of cross-linking and of derivatization was investigated. The thickening efficiency of a series of pre-gelatinized starches was compared. The features of the tested starches and their thickening efficiency are reported in the table below.

(17) Pre- Ag- Viscosity, Starting Alkylation Cross- gelatini-  
glomer- Condi- mPas, Sstarch Type linking zation ation tion  
45.degree. C. waxy hydroxy- yes.sup.1 spray- yes 1 4800 maize propyl  
dried.sup.2 2 15563 starch waxy hydroxy- yes.sup.1 spray- no 1 3738  
maize propyl dried.sup.2 2 13038 starch waxy hydroxy- yes.sup.1 drum-  
no 1 2738 maize propyl dried 2 6188 starch waxy none no spray- yes 1  
300 maize dried.sup.2 2 500 starch waxy acetyl yes.sup.1 spray- yes 1  
3325 maize dried.sup.2 2 2563 starch .sup.1 phosphorylated .sup.2  
according to U.S. Pat. No. 4,280,851

(92) The results show that the gelatinization process, cross-linking and alkylation had significant effects on thickening viscosity. Agglomeration appears to have a less significant effect on efficiency, although it does yield a performance advantage in terms of speed of dissolution. The spray dried pre-gelatinized, agglomerated, hydroxypropyl distarch phosphate was the most efficient starch derivative. The spray-dried, but not agglomerated, hydroxypropyl distarch phosphate was only slightly less efficient. A

large decrease in thickening efficiency was associated with pre-gelatinization by drum-drying. Apparently, the extra shear involved in this pre-gelatinization process degrades the starch, reducing its thickening efficiency. The chemical modifications were also critical to the viscosity build up. Virtually no viscosity build was observed with the unmodified spray-dried starch. The acetylated pre-gelatinized starch was significantly less efficient than the hydroxypropylated pre-gelatinized starch. As a whole, the above experimental results show that the most efficient starch thickener is the spray-dried hydroxypropylated distarch phosphate made from waxy maize starch.

**CLAIMS:**

What is claimed:

1. A composition which comprises a continuous aqueous phase comprising a pregelatinized, crosslinked starch selected from the group consisting of a C.sub.2 -C.sub.5 hydroxyalkyl starch and a C.sub.2 -C.sub.18 acyl starch, which composition is for cleaning or caring for skin, teeth, or hair or for cleaning smooth surfaces.
2. The composition of claim 1, wherein the starch is at least one starch selected from the group consisting of a hydroxypropyl di-starch phosphate, a hydroxypropyl di-starch C.sub.4 -C.sub.18 alkanate, and a hydroxypropyl di-starch C.sub.1 -C.sub.18 alkenate.
3. The composition of claim 2, wherein the starch is a hydroxypropyl di-starch phosphate and has an amylopectin content of at least about 70%.
4. The composition of claim 3, wherein the starch is a spray-dried starch.
5. The composition of claim 4, wherein the spray-dried starch comprises largely intact starch granules.
6. The composition of claim 5, wherein the spray-dried starch granules are agglomerated to loose aggregates.
7. The composition of claim 4, wherein the spray-dried starch is (i) a uniformly pregelatinized, granular starch in the form of indented spheres in which least a majority of the starch granules are whole and unbroken and in the form of loosely connected agglomerates or individual granules; (ii) a non-granular starch which is substantially non-crystalline, non-retrograded, and completely predispersed; or (iii) a mixture thereof.
8. The composition of claim 3, wherein the aqueous phase is about

5 to about 98 wt. % and the aqueous phase comprises about 0.1 to about 20 wt. % of the starch.

9. The composition of claim 3, wherein the aqueous phase further comprises at least about 0.3 wt. % of at least one surfactant selected from the group consisting of non-ionic, anionic, cationic, and amphoteric surfactant.

10. The composition of claim 9, wherein the surfactant is about 7 to about 25 wt. %.

11. The composition of claim 9, wherein the composition has a pH of between about 2.5 and about 12.

12. The composition of claim 11, wherein the pH is about 4 to about 9.

13. The composition of claim 3, wherein the composition further comprises at least about 1 wt. % of a hydrophobic phase.

14. The composition of claim 13, wherein the hydrophobic phase is finely dispersed and is about 5 to about 25 wt. %.

15. The composition of claim 14, wherein the hydrophobic phase comprises at least one compound selected from the group consisting of a liquid or a solid fatty acid monoester, a fatty acid diester, a fatty acid triglyceride, a hydrocarbon, an alkyl ether, an alkyl ethoxylate, an alkyl propoxylate, an alkyl butoxylate, a silicone, and a long-chain alcohol.

16. The composition of claim 13, wherein the composition further comprises about 0.1 to 10 wt % of an emulsifier.

17. The composition of claim 16, wherein the emulsifier is at least one emulsifier selected from the group consisting of a partial ester of a polyhydric alcohol, an ethoxylate, a propoxylate, and a butoxylate.

18. The composition of claim 3, wherein the composition is a gel.

19. The composition of claim 18, wherein the composition further comprises about 5 to about 25 wt. % of a monohydric alcohol and/or polyhydric alcohol.

20. The composition of claim 19, wherein the monohydric alcohol is ethanol and the polyhydric alcohol is glycerin.

21. The composition of claim 3, wherein the composition is a hair dyeing composition which further comprises a colorant.

22. The composition of claim 3, wherein the composition is a hair bleaching composition which further comprises an oxidizing agent.

23. A composition which is a two part hair dyeing composition or a hair bleaching composition, with one part comprising a pregelatinized, crosslinked starch selected from the group consisting of a C.sub.2 -C.sub.5 hydroxyalkyl starch, and a C.sub.2 -C.sub.18 acyl starch and the other component comprising an aqueous phase.

24. The composition of claim 23, wherein the starch component is a powdered starch.

25. A cleaning composition selected from the group consisting of a shampoo, a hair conditioner, a shower gel, a bath foam, a liquid soap, and a dental cream, which comprises an aqueous phase which comprises a pregelatinized, crosslinked starch selected from the group consisting of a C.sub.2 -C.sub.5 hydroxyalkyl starch and a C.sub.2 -C.sub.18 acyl starch and at least about 0.3 wt. % of a nonionic, anionic, cationic, or amphoteric surfactant.

26. The composition of claim 3, which further comprises an additive selected from the group consisting of a preservative, a perfume, a flavor, a light protection agent, an antioxidant, a vitamin, a filler, a sequestrant, a coloring agent, a bronzing agent, a thickener other than the starch, an inorganic salt, a pH-regulator and a luster agent.

27. The composition of claim 21, which further comprises an additive selected from the group consisting of a preservative, a perfume, a flavor, a light protection agent, an antioxidant, a vitamin, a filler, a sequestrant, a coloring agent, a bronzing agent, a thickener other than the starch, an inorganic salt, a pH-regulator and a luster agent.

28. The composition of claim 25, which further comprises an additive selected from the group consisting of a preservative, a perfume, a flavor, a light protection agent, an antioxidant, a vitamin, a filler, a sequestrant, a coloring agent, a bronzing agent, a thickener other than the starch, an inorganic salt, a pH-regulator and a luster agent.